November 1954 Pages 481 - 528

The Journal
of the
SOCIETY OF DYERS AND COLOURISTS

Volume 70 Number 11

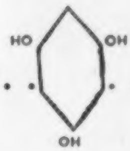
CONTENTS

THE SOCIETY OF DYERS AND COLOURISTS
19 PICCADILLY BRADFORD 1 YORKSHIRE

For chemists in the dyestuff industry

PHLOROGLUCINOL

from Whiffens



an interesting and versatile

developing agent for the

production of black dyestuffs

Apart from its main application in the production of black dyestuffs, this versatile chemical can be used to produce 'cold' blacks with superior light and perspiration fastness for acetate rayon. It compares favourably with beta oxynaphthoic acid and is 3½ times more efficient. Phloroglucinol is suitable for the preparation of blue acetate dyestuffs, and also for the dyeing of Nylon, wool and cotton.

IMMEDIATE DELIVERY EX-STOCK
For full information on the use of Phloroglucinol for this and other applications, write or telephone

WHIFFENS

fine chemicals for industry

WHIFFEN & SONS LTD., NORTH WEST HOUSE, MARYLEBONE ROAD, LONDON, N.W.1. TELEPHONE: PADDINGTON 1041/9
TELEGRAMS: WHIFFEN, NORWEST, LONDON

The Journal of the Society of Dyers and Colourists

(Subscription rates for non-members £4 per annum, post free)

(Abstracts section only printed on one side of paper— £1 10s 0d per annum)

NOTICE TO MEMBERS AND SUBSCRIBERS

Readers requiring *general information* regarding the Official Notices, List of Officers of the Society, etc. should consult pages 1–6 of the January 1954 and pages 262–266 of the July 1954 issues of the *Journal*, or write to *The Secretary*, The Society of Dyers and Colourists, Dean House, 19 Piccadilly, Bradford 1, Yorkshire (*Telephone* Bradford 25138–9). *Editorial Communications* should be addressed to *The Editor*, at the same address.

Forthcoming Papers

The following papers have been accepted by the Publications Committee, and will appear in future issues of the *Journal*—

LECTURES

The Behaviour of Leuco Vat Dyes at Temperatures greater than 100°C. — *S. Blackburn and M. R. Fox*

Continuous Ribbon Dyeing — *L. J. Clarke*

The Dyeing of Felt — *D. Haigh*

The Basic Mechanisms of Dye Absorption during Pad Dyeing — *H. B. Mann*

Affinity Effects during Padding — *W. J. Marshall*

The Principles governing the Efficiency of a Padding Mangle — *H. Potter*

COMMUNICATIONS

The Polarography of Azo Dyes — *J. de O. Cabral and H. A. Turner*

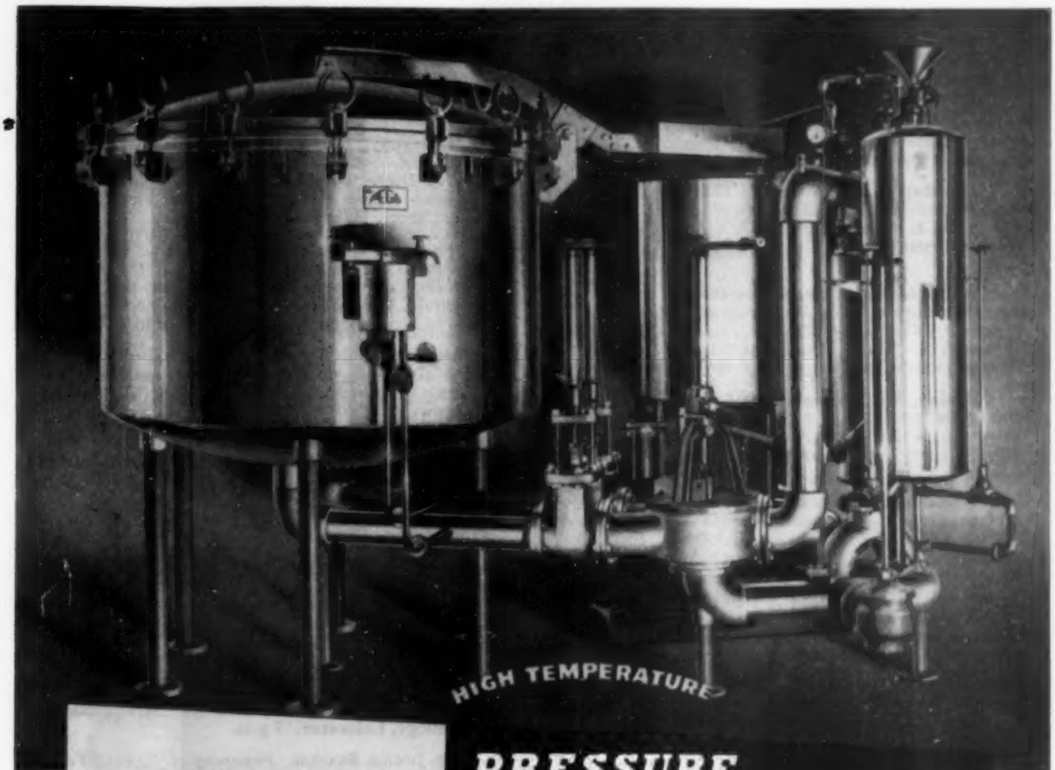
The Mechanisms of Some Reactions between *N*-Halogenoamines and Wool — *C. Earland*

Qualitative and Quantitative Analysis of Vat Dyes by Paper Chromatography — *E. Klingsberg*

Some Factors in the Measurement of Affinities of Vat Dyes for Cellulose — *R. H. Peters and J. Simons*

F.T.C.C. PUBLICATION

The Use of Fading Lamps for Determining Light Fastness — *K. McLaren*


HIGH TEMPERATURE

FORTHCOMING MEETINGS OF THE SOCIETY

Thursday, 25th November 1954

West Riding Section. *The Fixation of Direct Dyestuffs.* Dr. R. Gill (Allied Colloids Ltd.). Victoria Hotel, Bridge Street, **Bradford**. 7.30 p.m.

Friday, 26th November 1954

Bradford Junior Branch. *Colorimetry and Match Prediction.* E. Cowgill, Esq. (Messrs. I.C.I. Ltd.). **Bradford** Technical College. 7.15 p.m.

Tuesday, 30th November 1954

Leeds Junior Branch. *The Use of Physics in Dyeing Research.* E. Atherton, Esq., B.Sc. (Messrs. I.C.I. Ltd.). Departmental Lecture Theatre, The University, **Leeds.** 3.30 p.m.

Wednesday, 1st December 1954

Midlands Section. *The Evaluation of Optical Bleaching Agents.* G. G. Taylor, Esq., B.Sc., A.Inst.P. (Clayton Dyestuffs Co. Ltd.). (Joint meeting with the British Association of Chemists). College of Art, **Derby.** 7 p.m.

Friday, 3rd December 1954

London Section. *The Dyeing of Textile Fibres at Temperatures above 100°C.* J. A. Fowler, Esq. (I.C.I. Ltd.). Royal Society Rooms, Burlington House, **London, W.1.** 6 p.m.

Tuesday, 7th December 1954

Scottish Section. *Electrical Aids to Production in the Textile Industry.* L. Landon Goodman, Esq., B.Sc. (British Electrical Development Association). St. Enoch Hotel, **Glasgow.** 7 p.m.

Manchester Junior Branch. *A Comparison of Commercial Standards of a Crease-resist Finish on a Single Quality of Spun Rayon Fabric.* H. W. Best-Gordon, Esq. (Courtaulds Ltd., Droylsden). College of Technology, **Manchester.** 6.30 p.m.

Wednesday, 8th December 1954

Northern Ireland Section. *Some aspects of Design in Bleaching and Finishing Plant.* W. W. Spooner, Esq. (Spooner Dryer and Engineering Co. Ltd.). (Joint Meeting with Foremen Dyers' Guild). Thompson's Restaurant, Donegall Place, **Belfast.** 7.30 p.m.

Thursday, 9th December 1954

West Riding Section. *Oriental Printing Methods and Prints.* R. Thornton, Esq., B.Sc. (I.C.I. Ltd.). Victoria Hotel, Bridge Street, **Bradford.** 7.30 p.m.

Thursday, 16th December 1954

Bradford Junior Branch. *Special Finishes for Textiles and their Evaluation.* J. A. Potter, Esq., M.A., F.S.D.C. (Clayton Dyestuffs Co. Ltd.). **Bradford** Technical College. 7.15 p.m.

Friday, 17th December 1954

Manchester Section. *The Wear Properties of Resin Treated Fabrics.* Dr. T. H. Morton. Textile Institute. 6.30 p.m.

Tuesday, 21st December 1954

Huddersfield Section. *Printing of Wool, including Production of Melange Effects.* J. A. Potter, Esq., M.A., F.S.D.C. (Clayton Dyestuffs Co. Ltd.). The Co-operative Society Cafe, Buxton Road, **Huddersfield.** 7.30 p.m.

Thursday, 6th January 1955

Northern Ireland Section. *The Modern Approach to Linen Bleaching and Finishing* I. M. Hill, Esq. (Milltown Bleaching Co. Ltd.) (Joint lecture with Textile Institute). Thompson's Restaurant, Donegall Place, **Belfast.** 7.30 p.m.

Friday, 7th January 1955

London Section. *Cellulose Acetate and Water Repellency.* R. J. Mann, Esq., B.Sc. (British Celanese Ltd.). Royal Society Rooms, Burlington House, **London, W.1.** 6 p.m.

Tuesday, 11th January 1955

Bradford Junior Branch. Lecture. Title to be announced later (Messrs. S. Pegg & Son Ltd., Leicester).

Wednesday, 12th January 1955

Northern Ireland Section. *Application and Evaluation of Optical Bleaching Agents.* Messrs. G. G. Taylor, B.Sc., A.Inst.P., and G. Coe, A.M.C.T. (Clayton Dyestuffs Co. Ltd.). Thompson's Restaurant, Donegall Place, **Belfast.** 7.30 p.m.

Thursday, 13th January 1955

West Riding Section. *Can Dyeing Theory Aid the Practical Dyer?* Dr. L. Peters (Department of Textile Industries, Leeds University). The Victoria Hotel, Bridge Street, **Bradford.** 7.30 p.m.

Tuesday, 18th January 1955

Huddersfield Section. *Observations on the Dyeing of Wool at High Temperatures.* H. Sagar, Esq., A.T.I. (Imperial Chemical Industries Ltd.). The Co-operative Society Cafe, Buxton Road, **Huddersfield.** 7.30 p.m.

Scottish Section. *Hydrogen Peroxide Bleaching in the Textile Industry.* Messrs. L. S. Chesner and B. A. Standish (Laporte Chemicals Ltd.). St. Enoch Hotel, **Glasgow.** 7 p.m.

Friday, 21st January 1955

Manchester Section. Details later. Textile Institute. 6.30 p.m.

West Riding Section. Ladies' Evening. Victoria Hotel, Bridge Street, **Bradford.** 7.30 p.m.

Tuesday, 25th January 1955

Leeds Junior Branch. *Some Observations on the Dyeing of Wool at High Temperatures.* H. Sagar, Esq., F.R.I.C., A.T.I. (Messrs. I.C.I. Ltd.). Departmental Lecture Theatre, The University, **Leeds.** 3.30 p.m.

Wednesday, 26th January 1955

Midlands Section. *I do it this way!* Demonstrations of novel testing techniques by local members. College of Technology, **Leicester.** 7 p.m.

Bradford Junior Branch. *Processing of "Dynel" Textiles.* D. H. Stott, Esq. (Gemec Chemical Company). **Bradford** Technical College. 7.15 p.m.

Thursday, 27th January 1955

West Riding Section. *Some Aspects of Anthraquinone Dyestuffs Chemistry.* Dr. S. Coffey (Imperial Chemical Industries Ltd.). The Hotel Metropole, King Street, **Leeds.** 7.30 p.m.

Friday, 28th January 1955

London Section. Annual Dinner Dance at The Waldorf Hotel, **London W.C.2.**

Tuesday, 1st February 1955

Manchester Junior Branch. *Rates of Uptake of Vat Dyes by Cellulose.* Dr. R. H. Peters and Dr. T. Watson (Messrs. I.C.I. Ltd.). College of Technology, **Manchester.** 6.30 p.m.

Friday, 4th February 1955

London Section. *Textile Performance Standards for the Distributor.* Messrs. F. Cowles and J. S. Ingham (Marks and Spencer Ltd.). Royal Society Rooms, Burlington House, **London W.1.** 6 p.m.

Tuesday, 8th February 1955

Manchester Section. Joint meeting with the Textile Institute in Macclesfield. *The Dyeing Properties of "Terylene" Polyester Fibre.* J. G. Graham, Esq., B.Sc. Fuller details later.

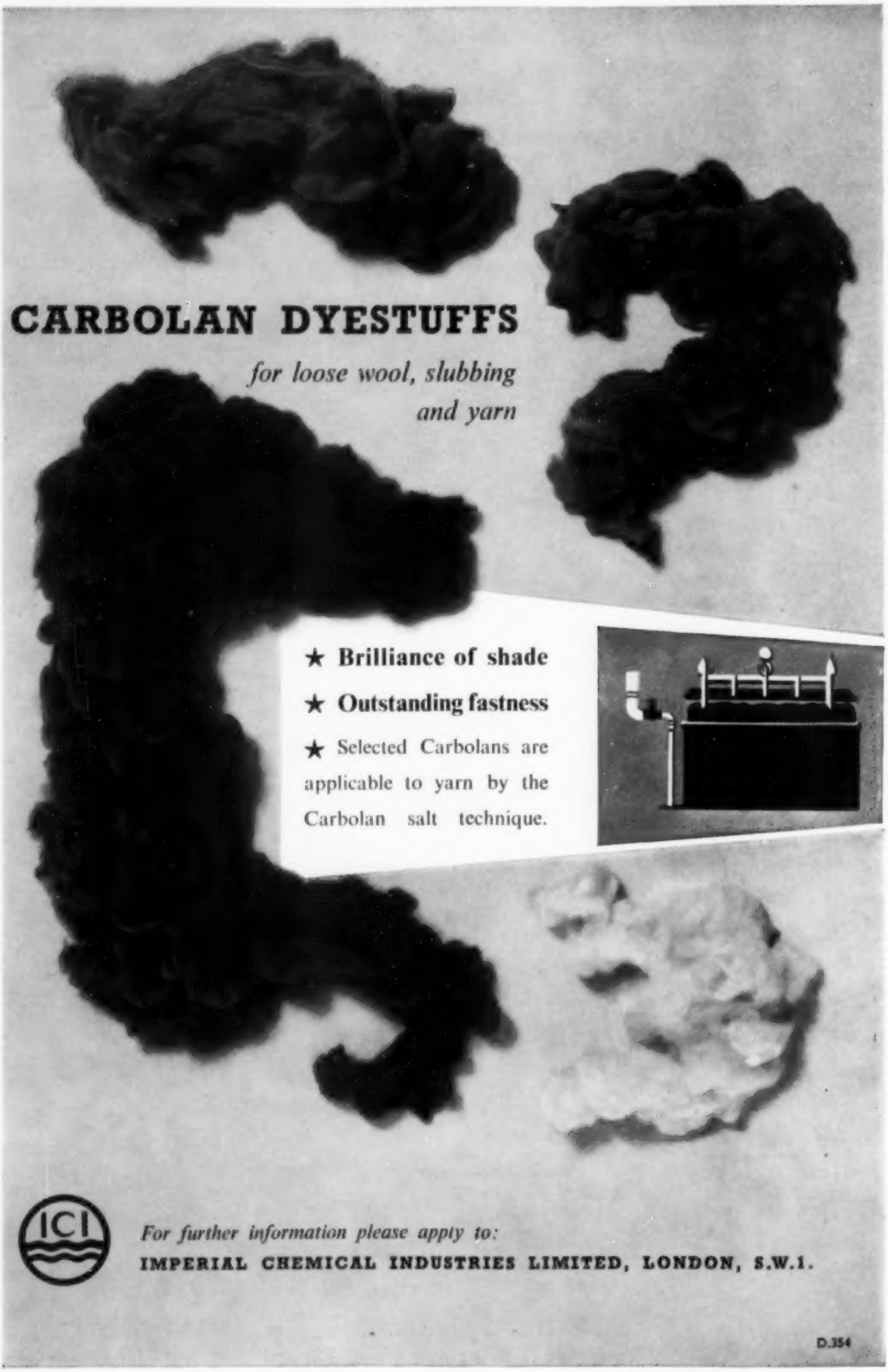
Leeds Junior Branch. *The Printing of Wool including the Production of Melange Effects.* J. A. Potter, Esq., M.A., F.S.D.C. (Messrs. Clayton Dyestuffs Co. Ltd.). Departmental Lecture Theatre, The University, **Leeds.** 3.30 p.m.

Wednesday, 9th February 1955

Northern Ireland Section. *Fastnesses of Coloured Textiles as they Affect the General Public.* J. S. Ingham Esq. (Marks & Spencer Ltd.). Thompson's Restaurant, Donegall Place, **Belfast.** 7.30 p.m.

continued on page xxxvii


SANDOZ
Colours for Wool
SPECIALITY
RANGES
for all
WOOL DYEING
requirements
Sandoz
PRODUCTS LTD.
BRADFORD


CARBOLAN DYESTUFFS
for loose wool, slubbing and yarn
★ Brilliance of shade
★ Outstanding fastness
★ Selected Carbolans are applicable to yarn by the Carbolan salt technique.
ICI
For further information please apply to:
IMPERIAL CHEMICAL INDUSTRIES LIMITED, LONDON, S.W.1.
D.354

THE JOURNAL

OF THE

Society of Dyers and Colourists

Volume 70 Number 11 — NOVEMBER 1954 — *Issued Monthly*

Proceedings of the Society

Some Applications of Organic *iso*Cyanates

G. S. J. White

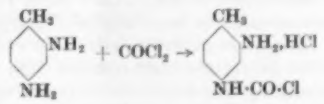
Meeting of the Manchester Section held at the Textile Institute, Manchester, on 2nd April 1954, Mr. J. Boulton in the chair

The preparation, properties, and reactions of organic *iso*cyanates are touched upon. There follows a review of their uses as adhesives, in lacquers, and in textile finishing. Other developments mentioned include the manufacture of elastic and rigid sponges and rubbers.

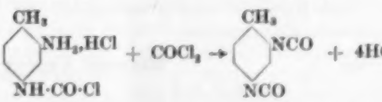
Although much of the chemistry of organic *iso*cyanates was known before 1910, it was not until thirty years later that important practical applications were investigated virtually simultaneously in this country, the U.S.A., and Germany; and manufacture began.

Manufacture

Many routes to *iso*cyanates are known, but only one is of commercial importance. Essentially, this consists in the reaction of an amine or an amine salt with phosgene in the presence of an inert medium (usually *o*-dichlorobenzene). Using *m*-toluylenediamine as an example, the reactions involved are as follows—



(i)



(ii)

Stage (i) generally proceeds rapidly at low temperatures (around 0°c.). Stage (ii) requires temperatures above 100°c., and is rather slow owing to the insolubility of both the hydrochloride intermediate and the phosgene in the solvent for the amine. In practice, therefore, this stage is carried out at reflux temperature with efficient agitation. The chief side-reaction occurs between a carbamoyl chloride or *iso*cyanate group and unchanged amine to give polyurea derivatives. In order to minimise this, Stage (i) may be conducted by addition of amine to excess of phosgene in a solvent at as low a temperature as possible. Urea formation can also be minimised by use of amine salts, but the salts of the weakly basic aromatic amines with strong acids are relatively insoluble, so that reaction is slow even at high temperatures. Aliphatic amines, however, give carbamates with carbon dioxide, and these are more soluble and react at a lower temperature than salts of aromatic amines. Phosgenation is complete when no more hydrogen chloride is evolved, and the crude *iso*cyanate is isolated by distilling off the solvent. If a pure *iso*cyanate of good colour is required, it is generally necessary to distil the crude product under vacuum, and this operation has to be carried out as quickly and at as low a temperature as possible because of the tendency of *iso*cyanates to polymerise on heating[1].

Properties and Reactions

A— REACTIONS WITH ACTIVE HYDROGEN COMPOUNDS

The most characteristic reactions of *iso*cyanates are those with active hydrogen compounds—

$$R{\cdot}NCO + HX \rightarrow R{\cdot}NH{\cdot}CO{\cdot}X$$

The reaction generally proceeds readily at ordinary temperature or after moderate heating without the use of catalysts. However, sodium, sodium alkoxides, tertiary amines, and Friedel–Crafts catalysts will catalyse most reactions of this type. A rough indication of the relative reactivities of some active hydrogen compounds is given below—

$$Alk{\cdot}NH_2 > Ar{\cdot}NH_2 > H_2O = R{\cdot}CH_2OH >$$
$$R^1R^2CHOH = R^1R^2R^3C{\cdot}OH > \text{Active } CH_2 > Ar{\cdot}OH >$$
$$R{\cdot}COOH > R{\cdot}CO{\cdot}NH_2$$

It should also be noted that the reactivity of an *iso*cyanate depends upon its type, the sequence of reactivity being—

$Ar{\cdot}NCO > R{\cdot}CH_2{\cdot}NCO > R^1R^2CH{\cdot}NCO > R^1R^2R^3C{\cdot}NCO$

Substituents such as nitro groups in the *ortho* or *para* positions of an aromatic *iso*cyanate enhance the reactivity, while groups such as methoxy reduce it.

Some details of the most important examples of this type of reaction are given below.

1— Hydrolysis

*iso*Cyanates are hydrolysed by water and, as indicated above, the aromatics are the most susceptible. The end-product may be a urea, an amine, or a mixture of the two, depending upon the conditions—

$$R{\cdot}NCO + H_2O \rightarrow R{\cdot}NH{\cdot}COOH \rightarrow R{\cdot}NH_2 + CO_2$$
$$R{\cdot}NH_2 + R{\cdot}NCO \rightarrow R{\cdot}NH{\cdot}CO{\cdot}NH{\cdot}R$$

Carbon dioxide is evolved in the first stage, and this reaction is utilised in the production of foamed polyester–*iso*cyanate plastics.

It is this ease of hydrolysis which necessitates considerable care in handling *iso*cyanates, since exposure to air will introduce moisture and cause separation of crystals of the corresponding substituted urea.

2— Primary Alcohols and Amine Derivatives

Primary alcohols react spontaneously with the formation of a urethan—

$$R^1{\cdot}NCO + R^2{\cdot}OH \rightarrow R^1{\cdot}NH{\cdot}COOR^2$$

This reaction is the basis of the formation of rubbers from di*iso*cyanates and polyesters containing hydroxyl end-groups, the difunctional molecules being linked together through the di*iso*cyanate.

Secondary alcohols, tertiary alcohols, and phenols react more slowly, but the reaction can be catalysed.

All compounds containing a hydrogen atom attached to a nitrogen atom will react—

$$R{\cdot}NCO + HN\langle \rightarrow R{\cdot}NH{\cdot}CO{\cdot}N\langle$$

For example, amines give ureas, amides give acylureas, and ureas give biurets. Amines generally react very much faster than amides or ureas.

3— Carboxylic Acids

*iso*Cyanates react with carboxylic acids to give amides and carbon dioxide—

$$R^1{\cdot}NCO + R^2{\cdot}COOH \rightarrow R^1{\cdot}NH{\cdot}CO{\cdot}O{\cdot}CO{\cdot}R^2$$
$$\rightarrow R^1{\cdot}NH{\cdot}CO{\cdot}R^2 + CO_2$$

This reaction, as well as that with water, is utilised in the production of foamed resins from di*iso*cyanates and polyesters carrying free carboxy end-groups.

4— Active Methylene Compounds

Acetoacetic ester, malonic ester, nitromethane, and other active methylene compounds condense with *iso*cyanates in the presence of sodium as a catalyst, e.g.—

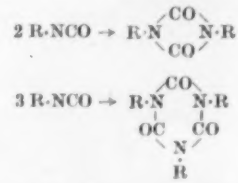
$$R{\cdot}NCO + CH_2(COOC_2H_5)_2 \rightarrow R{\cdot}NH{\cdot}CO{\cdot}CH(COOC_2H_5)_2$$

B— *ISO*CYANATE ADDUCTS

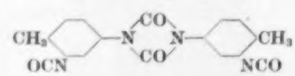
Many of the reactions of *iso*cyanates with active hydrogen compounds may be reversed by heating. This has been referred to in scientific literature as early as 1879 [2] and also more recently [3]. Reversal has been observed with hydrogen halides, amines, alcohols, phenols, sodium bisulphite, and active methylene compounds. The ease of regeneration is the inverse of the ease of formation. Often the reversal takes place only in the presence of a compound which gives a more stable product with the *iso*cyanates released. Thus it is possible to stabilise *iso*cyanates towards certain reactions, e.g. hydrolysis, at low temperatures, and yet obtain reaction at high temperatures.

C— POLYMERISATION

This is another general reaction of *iso*cyanates and one which at times is undesirable. Both dimers and trimers can be made—



Such polymerisation may be brought about by heat or by catalysts such as tertiary amines, sodium carbonate, sodium methoxide, and Friedel–Crafts catalysts. Toluylene di*iso*cyanate forms a dimer, the structure of which is probably—



and further polymerisation at the remaining free *iso*cyanate groups could build up a polymer of higher molecular weight. Aromatic *iso*cyanates can be regenerated from the dimers by heating. Dimers may give reactions similar to those of the free *iso*cyanates.

Hazards associated with the Use of *iso*Cyanates

The high reactivity of *iso*cyanates makes certain precautions essential in handling and using these chemicals. All suppliers stress, either on container labels or in the literature, that contact with skin or eyes and breathing of *iso*cyanate vapours must be avoided. The form of words employed by one manufacturer is as follows—

Warning **Harmful Vapour**

Avoid contact with skin and eyes.

In case of contact wash with soap and water.

For eyes give prolonged irrigation with water and get medical attention immediately.

Do not put water, solvent or other material into the container, or pressure may be generated.

It is known that *iso*cyanates of low molecular weight ($< 6C$) are lachrymators and that in general they may give rise to increased physical difficulty with asthmatic subjects. They may also be capable of producing dermatitis if handled casually. On the other hand, du Pont have reported in their literature [4] that diphenylmethane di*iso*cyanate is relatively non-toxic, and it is claimed [5] that the

tri*iso*cyanate contained in Desmodur R (FBy) is toxicologically not hazardous. It is certainly clear that the vapour hazard decreases with increasing molecular weight.

Uses

Apart from rubber applications, *iso*cyanates are normally employed in conjunction with chlorinated hydrocarbon solvents, which need careful control. Factories handling them must be adequately equipped with draughting hoods to enable work with *iso*cyanate-solvent systems to be undertaken safely, and this is undoubtedly a factor which has slowed down development in some industries.

The known uses may be summarised as adhesives, Vulcaprene, lacquers, foamed rubbers, foamed alkyds, and rubbers.

ADHESIVES

Textile–Rubber Bonding

The use of *iso*cyanates for bonding rubber to fabrics was developed during the 1939–1945 war. Diphenylmethane di*iso*cyanate was proposed as a bonding agent between rayon and natural and synthetic rubbers in 1943. At this time bonding agents based on latex, resorcinol, and formaldehyde resins were the main types of adhesive used by the tyre industry. However, the *iso*cyanate rayon-to-rubber bond is superior at high temperatures and after continued flexing. Diphenylmethane di*iso*cyanate was made available in this country in 1946 and since that time has been used in rubber solutions for bonding rayon tyre cord and in improving the bond between rayon or cotton and synthetic rubbers for belting and hose applications. It has also been used to bond nylon and Terylene tyre cords to natural rubber, and finds application in the manufacture of rayon, nylon, and Terylene proofings.

Triphenylmethane tri*iso*cyanate has also been recommended for both rubber-to-textile and rubber-to-metal bonding. Experiments on textile bonding indicate only marginal differences between di- and tri-*iso*cyanates. In the case of Terylene tyre cords, however, the tri*iso*cyanate gives more reproducible results in practice, and a product for this purpose was developed in 1951.

One restriction on the application of poly*iso*cyanates arises from the necessity to use organic solvents with accompanying fire hazards, possible toxicity, and recovery losses. The development of the acetoacetic ester adduct of diphenylmethane di*iso*cyanate in 1950 showed that products stable in water could be used in aqueous suspensions either alone or in combination with latex or in aromatic solvents to give high-strength rubber bonds to cotton and rayon. Unfortunately, this product cannot be used satisfactorily to bond rubber to nylon or Terylene. This *iso*cyanate adduct is inherently expensive, but it competes effectively with other *iso*cyanates or latex resorcinol–formaldehyde compositions, since small quantities yield very effective bond strengths.

Metal–Rubber Bonding

A technique has been developed for using diphenylmethane di*iso*cyanates for metal-to-rubber bonding [6]. This involves the use of a mixture of a compounded neoprene–chlorinated rubber and the *iso*cyanate in a solvent. Though it involves some special processing before the completed bonding agent is available for coating the metal, it gives superior results to traditional methods.

Miscellaneous Adhesives

The use of *iso*cyanates as adhesives in the boot and shoe industry is not large, but with the introduction of polyvinyl chloride leathercloth and high styrene–butadiene ($> 50\%$ styrene) rubber soles, with which they show good adhesion, it is probable that their use will increase. They will normally be applied along with Vulcaprene- or neoprene-based adhesives.

VULCAPRENE A—ADHESIVE AND LACQUER

Vulcaprene A is a rubbery polymeric ester–amide made from ethylene glycol, monoethanolamine, adipic acid, and hexamethylene di*iso*cyanate. It arose from research work by du Pont when looking for "rubbery nylons", but the du Pont contribution stopped at the raw rubber stage, and practical utilisation of the product derives from British inventions relating to curing of the polymer with *iso*cyanates and formaldehyde derivatives.

At the time of its discovery and for many years after, Vulcaprene A possessed unique properties which have encouraged its examination for a very wide range of applications. The properties of Vulcaprene may be summarised as follows—

1. A rubbery character with the ability to be fashioned and cured in a manner very close to the operations of the industries which process natural rubber. Such rubbers possess outstanding resistance to oils, petrol, ozone, and many solvents, and impermeability to gases, but suffer from poor hydrolytic resistance, including poor resistance to atmospheric moisture over long periods.

2. A high degree of self-adhesion and of adhesion to fibrous materials such as plied fabrics, leather and rubber in footwear, etc., including microcellular high styrene–butadiene synthetic rubbers, wood, and metals. Vulcaprene A may be cured at room temperature to a non-thermoplastic bonding layer by the addition of *iso*cyanates to the solution. This group of properties now accounts for the major use of Vulcaprene A. It can provide the bond between flock for artificial suèdes and the base material, although the hydrolytic stability may be a limiting factor in this use. Alkyd *iso*cyanates may also be used for this purpose to give bonds resistant to dry cleaning.

3. Miscibility with hard-film-forming materials, notably cellulose acetate, to give flexible and elastic lacquers of value on rubber proofings. This development may use the room-temperature *iso*cyanate curing system, though with heat curing no *iso*cyanate need be used. It provides an ozone-resistant layer easy to apply on rubber.

LACQUERS

When the first detailed work on the use of poly*iso*cyanates in the surface coating field was

reported [7], it was claimed that alkyds containing hydroxyl groups cured with poly*iso*cyanates have better adhesion, gloss, and resistance to solvents and mustard gas than conventional coatings. Work in Britain did not entirely support this [8], but did confirm that alkyd poly*iso*cyanates can form the basis of lacquers with remarkable adhesion, flexibility, and solvent and chemical resistance. Their possible use in the surface-coating industry has been widely explored.

The lacquers on rubber give films of good flexibility and very good gloss even at high pigmentation, and protect the rubber from degradation by ozone. The excellent solvent resistance makes them suitable for lacquering flexible rubber fuel tanks for aircraft.

Interest has also arisen in their use for lacquering leathers to give imitation patent leather, and on wood to give a surface of good solvent and scorch resistance. On linoleum these products impart appreciably greater wear resistance.

Polyvinyl acetate–polyvinyl chloride copolymers saponified to contain a small number of hydroxyl groups can be blended with alkyd resins and *iso*cyanates to give air-drying lacquers possessing superior adhesion to metal to the copolymer itself and yet retaining the chemical resistance of the vinyl resin.

Alkyds and *iso*cyanates blended with diphenylolpropane epichlorohydrin resins give films which, whilst retaining a good deal of the chemical resistance and toughness of this type of resin, can be cured to give flexible films at between room temperature and 100°C., instead of the 180°C. stoving temperature required when curing the epichlorohydrin resins along with urea–formaldehyde and phenol–formaldehyde resins. Their resistance to ester lubricants also makes them of interest in finishes for jet aircraft.

The use of polyester–*iso*cyanate and alkyd–*iso*cyanate lacquers for providing glossy abrasion-resistant finishes for high-quality polyvinyl chloride leathercloth is becoming established. Various firms are experimenting with these systems, the preferred *iso*cyanate for this application being diphenylmethane di*iso*cyanate.

ALKYD–POLY*ISO*CYANATES IN THE TEXTILE COATING INDUSTRY

The use of alkyd–poly*iso*cyanates to prepare rainproof garments and for some types of electrical fabrics was advocated by Bayer in 1941 [7]. When nylon parachute material became available in quantity just after the 1939–1945 war, a need arose for films having good adhesion to nylon fabric to allow an oilskin type of garment to be prepared in place of linseed oil proofing, which exhibits poor adhesion and flexibility on nylon. Development has proceeded, and now service tests on these products are in hand. Alkyd–*iso*cyanate-coated nylon and Terylene polyester fabrics have the following advantages over normal oilproofed material—

(i) Superior adhesion and flexibility

(ii) Much superior solvent and oil resistance

(iii) High abrasion resistance

(iv) No "stickiness" or "sweating back" on storage

(v) Resistance to boiling in soap and detergent solutions

(vi) Excellent flexibility after pigmentation.

The very good retention of flexibility and strength of alkyd–*iso*cyanate-coated Terylene fabrics after heat ageing for 700 hr. at 130°C. and 155°C. has prompted their development for the electrical industry. The oil and solvent resistance and the non-acidic extract from the films are other attractive properties. Although the electrical properties of such coated fabrics are good when high ratios of di*iso*cyanate are used, with lower ratios a poor power factor–temperature curve results.

TEXTILE FINISHING

As far as can be judged, two applications of poly*iso*cyanates for textile finishing have been extensively investigated. Their use to impart non-felting anti-shrink properties has been described by Speakman and co-workers [9] and by Krapa and Nyquist [10]. These processes do not appear to have been developed commercially. The second application relates to the use of poly*iso*cyanates for conferring stability on certain mechanical finishes and for reducing the water sensitivity of the more common textile fillers. Both the use of "solvent" solutions [11] and that of emulsions and dispersions [12] of poly*iso*cyanates are covered by patents. A number of poly*iso*cyanates have been examined in the laboratory. The best technical effect has been obtained with diphenylmethane 4:4-di*iso*cyanate and toluene 2:4-di*iso*cyanate–alkyd applied from "solvent" solution. Solvent applications gave the best results, inferior glaze retention being obtained with emulsions and with the water-soluble bisulphite adduct tested. Pretreatment of the fabric with a mildly basic compound such as urea or acetamide was found to be an essential part of the process. Although the treatment renders cellulose insoluble in cuprammonium hydroxide solution, only a slight improvement was obtained in the dimensional stability of viscose rayon fabric when treated with poly*iso*cyanates.

ELASTIC FOAMS AND SPONGES

It has already been mentioned that when *iso*cyanates react with organic carboxylic acids, or with water, carbon dioxide is evolved. When a polyester containing a proportion of acid end-groups is treated with a di*iso*cyanate, the chain-ends are linked together to form a high polymer, and carbon dioxide is simultaneously produced and trapped as bubbles in the stiffening plastic mass, giving a blown or foamed plastic. When substantially linear polyesters are used, elastic sponges are obtained resembling those from foamed latex. Instead of using acid-ended polyesters as a source of carbon dioxide, it is now preferred to use hydroxyl-ended polyesters and to add water, which links two molecules of di*iso*cyanate (and thus ultimately two molecules of polyester) with liberation of carbon dioxide and consequent blowing. The density of

the foam can be varied by altering the amounts of water and of di*iso*cyanate used. The simple polyesters, in conjunction with the polyester-di*iso*cyanate reaction products and a further proportion of toluylene di*iso*cyanate, give a series of products differing in resilience.

An important part of the manufacturing procedure is the rapid, thorough, and reproducible mixing of the ingredients, and a machine has been devised for this purpose. Large slabs are made and, after being trimmed to remove the surface skin, are cut up into pieces of the desired size.

Properties of iso*Cyanate Sponges*

The foams as normally prepared are straw to white in colour, depending on the colour of the raw materials and on the physical structure of the sponge: the finer the pore size, the nearer to white is the resultant material. Coloration is easy, and as no fillers are used, quite small amounts of pigments are all that are needed to give deep colours. Although the product is said to be flame-resistant, this is only relative, and samples continue to burn for a time after removal from the flame. They are, however, better than natural-rubber sponges in this respect, and could probably be improved to non-inflammability by the incorporation of flame-resistant plasticisers. In some respects the ageing properties of *iso*cyanate sponges are superior to those of natural rubber foams, but in others they are inferior. Thus, they have excellent resistance to the action of oxygen and ozone, and accelerated tests have shown that samples are virtually unchanged by conditions which bring about almost complete breakdown of rubber sponges.

Exposure to steam, however, degrades some of these products fairly rapidly; e.g. after about 50 hr. in low-pressure steam the "snap" is beginning to fall off, and after 70–90 hr. the material is of no further value as a sponge, whereas rubber latex foams are almost unaffected by this treatment. On the other hand, immersion in water does not appear to be deleterious, and *iso*cyanate foams withstand the effects of warm soap solution for prolonged periods. To solvents and oils, *iso*cyanate foams are more resistant than natural rubber: swelling occurs in some chlorinated solvents, but less than in the case of rubber; mineral and vegetable oils which rapidly attack rubber are almost without effect.

The physical properties of the *iso*cyanate foams and natural-rubber foams are similar except for the very low density of the *iso*cyanate foams.

*iso*Cyanate sponges are suitable for application as mattresses, upholstery, and washing sponges. Carpet underlays, toys, footwear, and packaging materials are other potential uses, whilst their insulating properties for sound and heat suggest outlets in the manufacture of light-weight blankets and Arctic clothing.

Rigid Foams

Rigid foams can be made by interaction of a poly*iso*cyanate and an alkyd resin containing sufficient carboxyl groups, or in the presence of water, to provide carbon dioxide for blowing. They were developed in Germany during the war, their potential usage in aircraft construction having been examined by the Luftwaffe as early as 1941. The chief value of such foams is that they can be formed *in situ*; i.e. they can be poured or pumped as a liquid (if necessary through a narrow aperture) into a cavity, and will then give a rigid foam without the application of heat, gas, vacuum, or pressure. After the war the Goodyear Aircraft Corpn. investigated this type of material under a contract from the U.S. Government. The Lockheed Aircraft Co. evaluated these materials, and have been granted a number of U.S. patents [13]. Their main use is in aircraft to obviate defects of the all-metal construction. The present method of using riveted metal supports in the wings not only is expensive but the "quilting" effect on the wing surface due to the protruding rivets affects the flying performance. The use of foamed alkyds inside an aluminium skin gives adequate strength with a smooth wing surface, and is also more economical in manufacture. At the same time, resistance to break-up of the wing by cannon shells is greatly improved. Uses for the foamed alkyds may also develop as floats for pontoon bridges and unsinkable boats. Uses in thermal and sound insulation (particularly in ships) and as void fillers to exclude moisture and other undesirable substances have also been suggested.

*ISO*CYANATE RUBBERS

During 1940–1942 various investigations by du Pont, I.C.I., and Dynamit A.G. showed that rubbery polymers were formed when certain polyesters were treated with di*iso*cyanates. These particular rubbers had several defects and, with the exception of Vulcaprene A, were never developed. Bayer, who had been working on *iso*cyanate chemistry for some years, took up the study of such rubbers, especially those made from linear polyesters such as polyethylene adipate. He showed (1945–1947) that the structure of the *iso*cyanate used was of critical importance. Hexamethylene di*iso*cyanate gave products which hardened at once, and toluylene di*iso*cyanate did not give satisfactorily cured rubbers. A number of less accessible di*iso*cyanates, however, gave rubbers with outstandingly good properties, much superior to natural and other synthetic rubbers in tensile and tear strength, and abrasion, oxidation, and oil resistance. Of these, naphthylene 1:5-di*iso*cyanate was preferred. Of polyesters, polyethylene adipate gave the rubbers with the best physical properties, and although the name "Vulkollan N" is used in technical literature to cover a variety of ester-*iso*cyanate rubbers of this type, it appears to refer mainly to rubbers made from these two compounds. These rubbers harden on standing, and although the onset of this defect can be delayed by using a polyester of molecular weight 1800–2800, it has not been entirely prevented. A full account of the early history of this development is given by Bayer [14]. The processes as described were not adaptable to bulk manufacture of rubber-like

articles, and there was no commercial development at that stage. Bayer then devised alternative processing techniques [15]. The polyester–*iso*cyanate reaction product is treated with a glycol (instead of water, which was used in the earlier "crumb" process), and the mixture heated to effect the cure. This process lends itself particularly to the casting of articles in moulds.

In a typical "casting process", the carefully dried polyester and naphthylene 1:5-di*iso*cyanate are mixed and heated in a stirred vessel, and when the reaction is complete a small amount of a glycol is added. The mix is initially fluid, but as the viscosity increases rapidly it is poured quickly into appropriate moulds. These are heated for 1–2 hr. at about 110°C., when the castings are removed and the cure is completed by further heating, e.g. at 110°C. for 12 hr. Alternatively, the polyester–di*iso*cyanate–glycol reaction product may be allowed to become more viscous and then may be worked on a rubber mill to a rough sheet, which yields moulded articles by conventional methods.

Wingfoot–Goodyear are also working in this field, and in the Summer of 1953 they announced "Chemigum SL", which is an ester–*iso*cyanate rubber [16].

The extent of the commercial development of these *iso*cyanate rubbers is not clear at present. Although there is plenty of interest in Europe in their potentialities, there is little information on the manufacture or sale of fabricated articles. Mention has been made in the German technical press of a solid trolley tyre and a "veneered" natural-rubber car tyre, which are stated to have at least twice the life of natural-rubber tyres.

In use, the high resistance of the *iso*cyanate rubber to abrasion could give a tyre of superior performance, but any subsequent hydrolysis would bring about the onset of cold-hardening with loss of resilience and decreased resistance to abrasion.

Conclusion

This has been a very brief review of the properties and applications of the organic *iso*cyanates. It will have served its purpose if it has revealed their interesting chemical potentialities to all who are concerned with the tinctorial and allied arts.

* * *

My thanks are due to my colleagues in the research and technical service departments of the Dyestuffs Division who have aided me in the preparation of this paper.

IMPERIAL CHEMICAL INDUSTRIES LTD.
DYESTUFFS DIVISION
HEXAGON HOUSE
MANCHESTER 9

(*MS. received 3rd May 1954*)

References

1 Hill, R. (editor), *Fibres from Synthetic Polymers* (Amsterdam: Elsevier, 1953), pp. 161–165.

2 Braumer, *Ber. dtsch. chem. Ges.*, **12**, 1874 (1879).

3 *BIOS* 719 and 1472.

4 DuP, *Report* No. 47–4, p. 19 (1947).

5 Fromandi, *Rubber Age and Synthetics*, **33**, 521 (1953).

6 ICI, *BP* 604,834.

7 *CIOS* XXIX–12 (Appendix).

8 Waters and Robinson, *J. Oil & Col. Chem. Assocn.*, **34**, 361 (1951).

9 Barr, Capp, and Speakman, J.S.D.C., **62**, 338 (1946).

10 Krapa and Nyquist, *USP* 2,468,716.

11 Bradford Dyers Assocn., *BP* 696,029.

12 Idem, *BP* 696,030.

13 Lockheed Aircraft Co., *USP* 2,577,279–81, 2,591,884, 2,602,783.

14 Bayer *et al.*, *Angew. Chem.*, **62**, 57 (1950).

15 Bayer *et al.*, *ibid.*, **64**, 523 (1952).

16 Seeger, Mastin, Fauser, Farson, Finelli, and Sinclair, *Ind. Eng. Chem.*, **45**, 2538 (1953).

Discussion

Mr. R. THORNTON: Would the lecturer care to make any comment on the heat-insulating properties?

Mr. WHITE: Alkyd–*iso*cyanate foams have good thermal insulation properties. The figures published vary according to the density and the structure of the foam but appear to be approximately equal to those of granulated cork. It must be borne in mind that these structures soften at approx. 140°C.

Mr. J. GREENWOOD: Have these products any electrical insulation properties?

Mr. WHITE: They are non-conductors and at high frequencies have good electrical properties. They may find application along with Terylene fibre in electrical apparatus developing moderate temperatures during use.

Dr. P. KRUG: Is it correct that the Helizarine (Basf) pigment compositions are based on *iso*cyanate chemistry?

Mr. WHITE: The actual constitution of the compositions mentioned is highly complex and, so far as I am aware, there is no published information on this subject. There are, however, patents in the field which mention the employment of *iso*cyanates.

Mr. C. P. ATKINSON: I understand that an American claim for the advantages of the treatment of fabrics with di*iso*cyanates is one of reduced swelling, and that therefore the final finishes are less affected by wetting and hot soaping processes. May this be of interest in connection with Everglaze-type finishes?

Mr. WHITE: The finishes obtained on cotton and rayon by the application of *iso*cyanates do tend to change the reactivity of the fibre to water and water vapour. So far as they are related to the finish named by the questioner, they appear to give results between that and the urea–formaldehyde process. Their resistance to washing is superior to the latter.

COMMUNICATIONS

The Influence of the Substrate upon the Light Fading of Azo Dyes

H. R. CHIPALKATTI, N. F. DESAI, C. H. GILES, and N. MACAULAY

Several series of simple phenylazonaphthalene dyes, both water-soluble and water-insoluble, have been applied to a variety of substrates, and the relative fading rates of the dyes in each series on each substrate have been compared with the Hammett σ-values of *meta* and *para* substituents in the benzene nucleus. The fading rates on transparent substrates were measured spectrophotometrically and those on opaque substrates by visual judgment, the two procedures giving concordant results. The conclusions reached may be summarised thus—

(*a*) All the substrates used fall distinctly into two classes, according to the sense in which they influence the relative fading rates, viz. (i) proteins, i.e. wool, silk, and gelatin; and (ii) all other materials, including cellulose, cellulose esters and ethers, and nylon.

(*b*) The protein substrates may perhaps take part chemically in the fading reaction, probably by reduction of the dye. The reaction does not appear to involve either the peptide linkages or the hydrocarbon portions of the protein molecules, but may perhaps involve the tyrosine or histidine side-chains.

(*c*) The non-protein substrates may perhaps not take part, chemically, in the fading reaction, which is considered to be oxidative in the absence of protein.

(*d*) Differences in the light fastness of any dye on different substrates of the same class are attributable largely to differences in its state of dispersion, determined by the physical nature of the substrates.

Introduction

It is well known that the light fastness of any given dye may vary considerably according to the fibre to which it has been applied, but little effort has previously been made to account for the variations observed or even to attempt to classify and systematise them. The present paper describes some preliminary investigations designed to determine whether any systematic variation of fastness between different substrates can be detected, and if so, whether the underlying cause of the variation can be found.

The method used is based essentially on those first described by Kienle, Stearns, and van der Meulen [26] and later by Atherton and Seltzer [3] and Atherton and Peters [2], who studied the fading of phenylazonaphthalene dyes containing simple substituents in the benzene nucleus. They measured the fading of each member of the series relative to that of the unsubstituted dye, and determined the relationship to the Hammett σ-values* for the respective substituent groups. Kienle *et al.* used water-soluble dyes derived from aniline coupled with 2-naphthol-3:6-disulphonic acid (R acid), in gelatin film, and Atherton *et al.* used water-insoluble dyes derived from aniline coupled with α-naphthylamine, in films of cellulose acetate. In both cases a linear relationship was noted between the σ-value and the relative fading rate, but Kienle *et al.* obtained a line of positive slope and Atherton *et al.* one of negative slope. Desai and Giles [13] had also detected a qualitative relationship between the fading rates of some water-insoluble azo dyes on cellulose or in oil media which is in the same sense as the relationship found by Atherton *et al.*

The present work was undertaken in order to extend such observations to a much wider range of substrates and to some other series of azo dyes, the purpose being to discover whether any systematic influence of the substrate upon the course of light fading is detectable, and if so, what is its fundamental cause; further, it was hoped that the results would show whether the apparent inconsistency between the results of the earlier investigators could be attributed either to the effects of the substrates or to the variation in the constitution of the dyes used.

Two series of dyes have been used for most of the present experiments, viz. water-soluble phenylazo-R acid dyes and water-insoluble phenylazo-β-naphthol dyes; some other dyes have also been included in a few tests. The experiments may be divided broadly into two classes according to the method used for determining fading, viz. (*a*) spectrophotometric measurement, used with dyes in transparent substrates, and (*b*) visual estimation, used with dyes on opaque substrates.

The spectrophotometric procedure of course gives the more precise results, but the visual method is found nevertheless to give results in good agreement with it, and the use of this method has also enabled the general conclusions to be confirmed by the use of a wider range of substrates.

EVIDENCE OF OXIDATION AND REDUCTION OF DYES IN FADING

As a necessary preliminary to the discussion of the present results it is desirable to review the evidence of earlier investigators showing that dyes may suffer oxidation or reduction when irradiated.

Oxidation

There is a good deal of evidence, all of it obtained from work on cellulosic substrates, that oxidation of the dye probably accompanies fading. This evidence has been obtained e.g. from the examination of fading products [12,19,23,30]; from the behaviour of oxidising agents as sensitisers and of reducing agents as restrainers of fading [30]; from the fact that substituent groups in azo dyes which increase resistance to oxidation also increase resistance to fading, and those which lower resistance to oxidation have an adverse effect on light fastness [13]; and from the fact that fading does not occur in absence of oxygen [17,21,27], though this is not necessarily firm proof that fading is itself an oxidation process.

* The σ-value is defined as the logarithm of the ratio of the ionisation constant of the benzoic acid containing the particular substituent group to that of the unsubstituted acid. Values for only *meta* and *para* substituents can be determined [20].

Relation between Relative Fading Rate and σ-Value

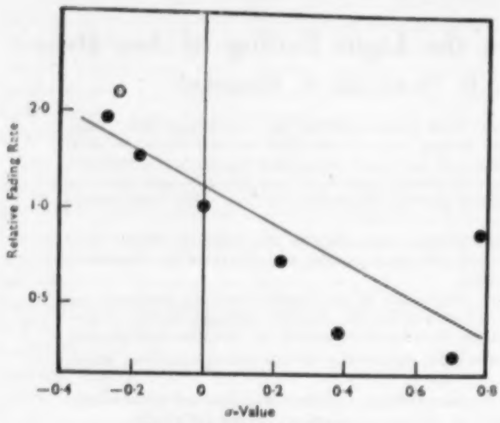


FIG. 1— Anodised Aluminium

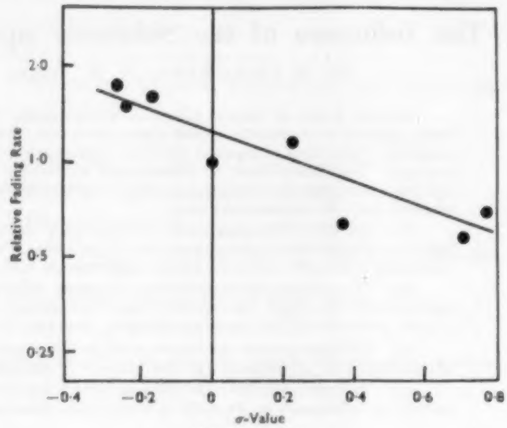


FIG. 2— Asbestos

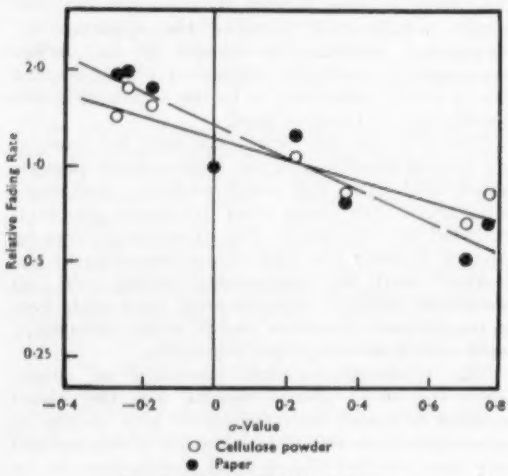


FIG. 3— Cellulose Powder and Paper

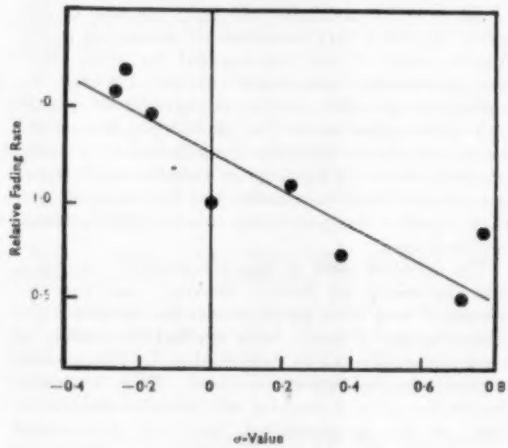


FIG. 4— Cotton

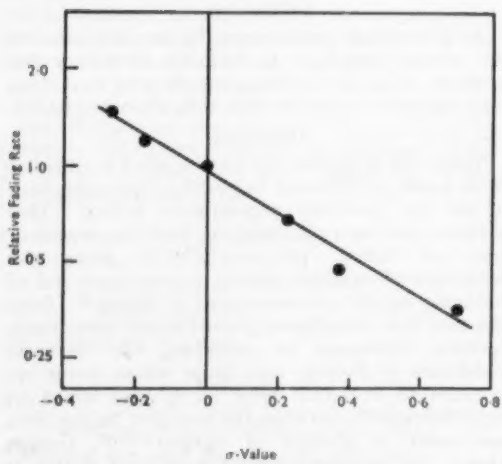


FIG. 5— Collodion

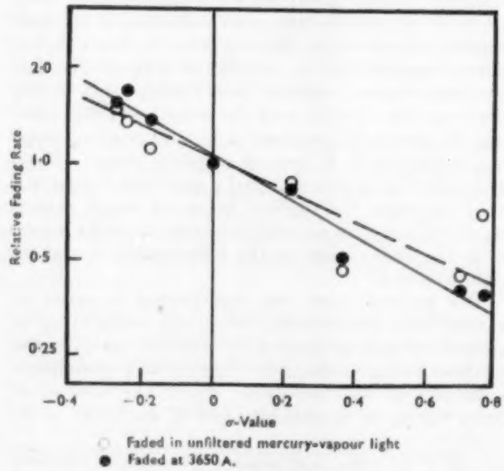


FIG. 6— Methyl Ethyl Cellulose

Reduction

Very little has been reported regarding reduction of dyes during fading, though some investigators have made observations suggesting that individual substituent groups in dyes are reduced on irradiation [2,21,30,35]; also some basic dyes on cotton appear to be reduced when exposed to short-wave ultraviolet radiation, the fibre being oxidised [21]. It is well known, however, that potassium dichromate is reduced to chromic salts when irradiated in gelatin, which is thereby insolubilised (tanned). This reaction has been known for over a century, and is in fact the basis of the very important industry of the photomechanical reproduction of illustrations. A number of investigations upon it have been reported [4,10,15,16], but it does not appear that the mechanism is fully understood.

Evidence from the Becquerel Effect

A current can be produced by illuminating a platinum electrode coated with an adsorbed dye. This so-called Becquerel effect has recently been investigated by Hillson and Rideal [24], who found that either oxidation or reduction of azo or triphenylmethane dyes can occur during irradiation of the electrode, according to the experimental conditions. The two reactions may proceed independently of one another.

Results and Discussion

The results are summarised in Table I, and it is seen at once that the substrates may be divided into two distinct classes, according to the sign of slope of their regression line. The protein substrates give lines of positive slope, and the non-proteins lines of negative slope. As a working hypothesis, it is therefore assumed that the fading reactions which occur on these two classes of substrate are fundamentally different in nature, and possible reasons for this are discussed below.

First, however, it is desirable to consider the significance of the differences between lines of the same sign of slope, and the nature of the principal experimental errors.

SOURCES OF ERROR

The individual points are scattered to various extents about the regression lines (which were calculated by the least-squares method). The scatter is largely due to random rather than to systematic errors, because it is considerably reduced by irradiating replicate sets of specimens and plotting the mean values for each dye. The points actually shown in Fig. 1–4 and 6–12 were obtained in this way. It is to be expected that a principal source of error in the specimens examined visually will be the difficulty of judging the extent of fading by eye, and indeed, in confirmation of this, the results obtained by spectrophotometric measurement do show better consistency. Yet even the spectrophotometrically determined results both in this work and in that of the earlier investigators are not entirely free from random errors.

TABLE I

Relationship between Substrate, Nature of Dye, and Slope of Regression Line of Relative Fading Rate on σ-Value of Substituent Group

Substrate	Dye*	Solubility†	Coloration‡	Determination§	Slope‖	Fig. No.	t**
NON-PROTEIN							
Anodised aluminium	R acid	s	d	V	−1·9	1	150
Asbestos	R acid	s	d	V	−1·4	2	110
Cellulose (paper)	R acid	s	d	V	−1·7	3	160
Cellulose (powder)	R acid	s	d	V	−1·1	3	150
Cellulose (cotton)	R acid	s	d	V	−1·9	4	220
Cellulose acetate [3]	α-Naphthylamine	i	c	S	−1·3	—	—
Cellulose acetate [3]	α-Naphthylamine	i	c	S	−3·3	—	—
Collodion	β-Naphthol	i	c	S	−2·1	5	110
Methyl ethyl cellulose	R acid	s	c	S	−2·3	6	410
Nylon	R acid	s	d	S	−1·8	7	640
Polyglycine	R acid	s	d	V	−1·7	8	120
Various non-protein	Various naphthols††	s, i	d	V	−1·3	12	—
PROTEIN							
Gelatin	R acid	s	c	S	+0·4	9	4170
Gelatin [26]	R acid	s	d	S	+2·3	—	—
Silk	R acid	s	d	V	+0·9	10	—
Wool	R acid	s	d	V	+1·0	11	—
Wool [26]	R acid	s	d	S	+2·3	—	—

* Aniline and derivatives diazotised and coupled with component indicated.

† s = Soluble in water; i = Insoluble in water.

‡ Method of coloration: d = Application by dyeing or padding; c = Incorporation in liquid dope.

§ Method of determination: V = Visual; S = Spectrophotometric.

‖ Units used for slopes are: *Ordinates*— Multiples of two in relative fading rate, or one *B.S.* 1006 grade; *Abscissae*— One unit of σ-value. Slopes for other investigators' lines have been recalculated on this basis from original diagrams.

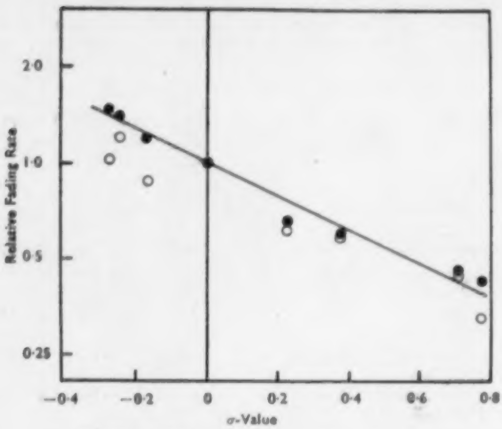
** t = Mean time (min.) for measured fade of aniline derivative (10% loss for S §; just perceptible fade for V §) (400-watt lamp).

†† See Table VI.

It will be the purpose of a later paper to show that the light fastness of most dyes is considerably influenced by their state of physical dispersion in the substrate, and it was considered that in the present work much of the random error not accounted for by difficulties of measurement might perhaps be attributable to this cause, originating possibly in small variations in the conditions of drying. It had also been observed, and this also will be reported later, that some water-insoluble dyes appear to be more uniformly dispersed in films of collodion than in other substrates. Accordingly, this material was examined in the present series as a substrate for water-insoluble dyes, and a remarkable freedom from random error was observed in only a single run (Fig. 5).

This seems to confirm that the principal sources of error in the present method lie in the non-uniform physical state of the dyes in the substrates, and, in the case of visually tested materials, in the

Relation between Relative Fading Rate and σ-Value



● Direct values

○ Values calculated on basis of equivalent absorption

(Least squares line for direct values)

FIG. 7 — Nylon

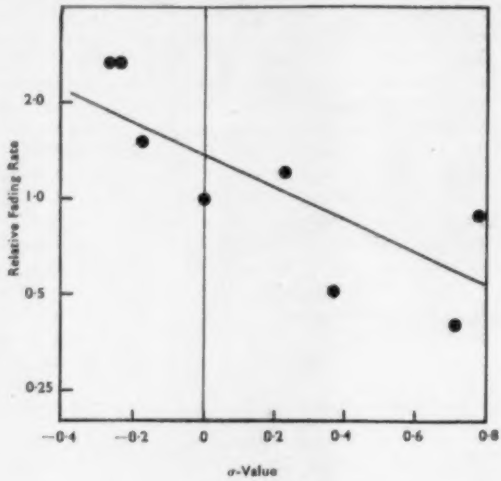


FIG. 8— Polyglycine

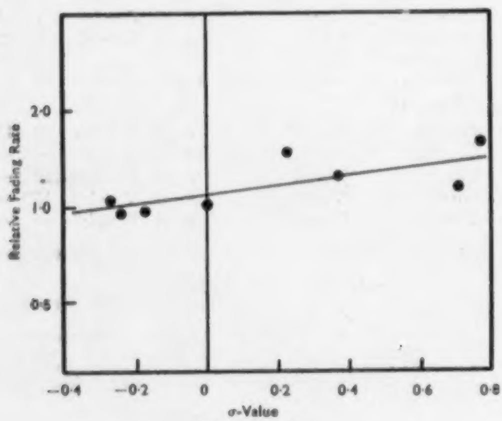


FIG. 9— Gelatin

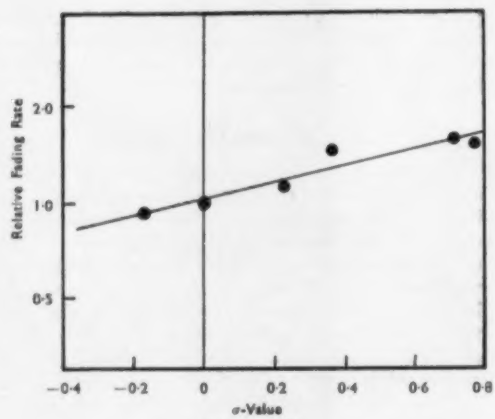
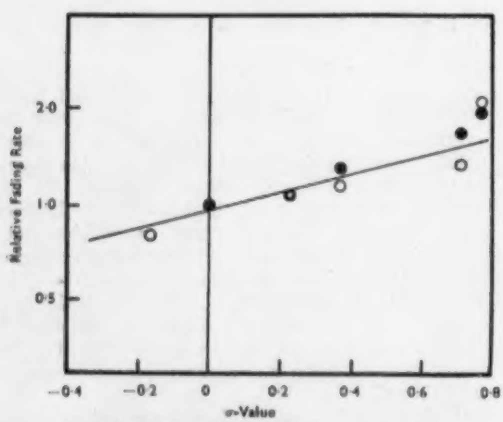


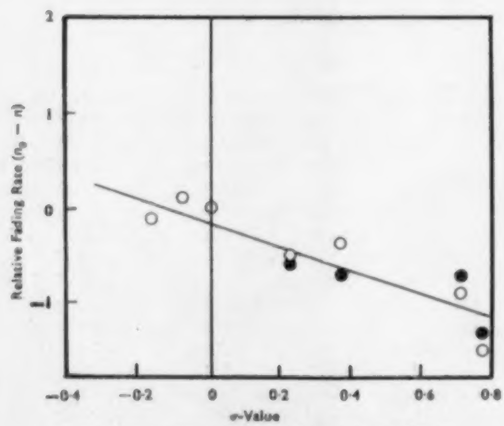
FIG. 10— Silk



○ Acid, alkaline, and neutral conditions; mean results

● Over pyruvic acid

FIG. 11— Wool



○ Grand mean values, various o-hydroxyazo dyes (Table VI, columns i–v)

● Brenthol dyeings on Cotton (Table VI, column vii)

FIG. 12

difficulty of judging the extent of fading. There is no evidence that the nature of the illumination or the environmental conditions of fading are at all important in comparison with these other factors.

SIGNIFICANCE OF SLOPE DIFFERENCES

The differences in slope may be divided readily into those of sign and those of magnitude. The former are distinct and leave no doubt as to the classification of the substrates. The latter are less readily interpreted; it is believed, however, that they may be accounted for by differences in the average state of aggregation of the dyes in the substrates. In this connection it will be observed (Table II) that there is a fairly consistent tendency for the slopes of both substrate classes to be more positive in the case of dyed or padded materials than in those of films cast from coloured liquid dopes. This applies to protein and non-protein substrates alike, and it suggests that two superimposed factors may be influencing the slopes — (*a*) the chemical nature of the fading reaction, which affects only the sign of slope; and (*b*) the physical environment during the initial drying of the coloured substrates, which affects the magnitude of slope, by influencing the physical form of the dyes. When the dye is incorporated in a liquid dope there is less possibility of its crystallising during drying than when it is dyed or padded on a solid material, because as drying of the dope proceeds the individual dye molecules will become trapped in molecular chains of the film-forming material. Thus the dye particles in a dope-coloured film should be smaller than in a normally dyed one; in the former the dye in fact may be almost in a solid solution, i.e. a random arrangement of film polymer molecules and entrapped individual dye molecules.

TABLE II

Relation of Slope to Method of Coloration

Method of Coloration	Slopes	
	Non-proteins	Proteins
Dyeing or padding ...	−1·9 to −1·3	+0·9 to +2·3
Incorporation in dope ...	−3·3 to −2·1	+0·4

If this interpretation is correct, then, according to the data summarised in Table II, the larger the particles of dye which are faded, the more positive is the slope of the regression line. In any dyed substrate the solid particles will not, of course, be of uniform size: there will probably be a random size distribution. On irradiation, if fading occurs only at the surface of particles*, the smallest will disappear first and the largest last. Thus, if the magnitude of slope is a function of particle size, it should vary with the proportion of dye faded when the assessments are made, and it should thus become more positive with increase in that proportion. No specific tests have been made to check this hypothesis, but it is perhaps confirmed by the relative values of the slope for the same series of dyes on wool as measured here (+ 1·0) and by Kienle *et al.*[26] (+ 2·3), because in this work the fading was judged at a much earlier stage, viz. 10–20% total loss of dye, than that used by Kienle *et al.*, who faded their specimens to the extent of ca. 50% loss of dye.

* Experimental evidence for this will be given in a later paper.

To summarise, differences in average degree of aggregation of all the dyes of any one series, as between substrates, cause differences in magnitude of the slope of the respective regression lines, but not in its sign. Differences of the same nature, as between individual dyes of any one series on a given substrate, however, cause random scatter of points about the lines.

There is no evidence that these physical influences are in any case sufficient to affect the sign of slope, which must therefore be determined solely by the chemical nature of the fading reaction.

It should be stated that Atherton and Seltzer[3] obtained their slope value of −1·3 from a series of dyes including two with nitro groups. Later, Atherton and Peters[2] examined additional dyes, including chloro derivatives, and found that the nitro compounds, and one other (containing an acetyl group), gave points well away from the best line for the remainder. The anomalous results they attributed to possible reduction of the substituent groups during fading. In the present work, both chloro and nitro compounds are included, and all seem to give points on the same regression lines.

NATURE OF FADING REACTION ON NON-PROTEIN SUBSTRATES

The explanation of the similarity in behaviour of the non-protein materials which seems to accord best with all the facts is that fading is an oxidation and that it may not involve any chemical reaction with this class of substrate. On the one hand, it seems unlikely that quite inert materials like porous clay tile or asbestos, or even methyl ethyl cellulose, can take part chemically in the fading; and on the other, there are some grounds for believing that in cellulose the molecular chains in the regions accessible to dyes are surrounded by firmly bound water molecules and do not come into direct contact with dye molecules[1a]. Therefore, it seems that an excited dye molecule in cellulose, being in direct contact with water and not with cellulose, may pass on its energy only to the former. If this is so, then the substrate serves solely as an inert surface on which the dye is spread. Differences in the absolute fading rate of a given dye between substrates of this general class may then be ascribed solely to the differences in porosity, which affect the degree of spreading of the dye on the internal surface and so influence the magnitude of the interface it exposes to the air, and which may affect also the rate of diffusion of oxygen or moisture required for the fading reaction. The dyes used in this work have little or no affinity for these non-protein substrates, so that when the bulk of the solvent has evaporated they will separate as crystals or as amorphous aggregates. Even if some chemical bonding between dye and substrate does operate in presence of the solvent, this may be disturbed in favour of aggregation of the dye molecules when the solvent evaporates.

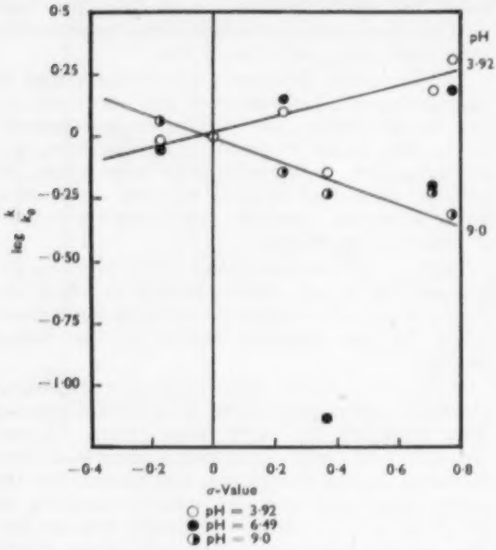


FIG. 13—Relation between Relative Oxidation Rate and σ-Value

In illustration, we may point to the difference between the fastness of two series of dyes on porous tile (Table VI). Those in the unsulphonated series, which separate from solution readily as fairly large crystals, have much higher fastness than the corresponding sulphonated dyes, which will separate probably as amorphous aggregates, and thus expose a greater surface area to the air. It is unlikely that the difference can be attributed to any difference in chemical reactivity of the individual dye molecules as between the two series, because the sulphonic acid groups are not situated in positions which can readily influence the reactive centre, i.e. the azo group.

NATURE OF FADING REACTION ON PROTEIN SUBSTRATES

Whether or not non-proteins take part in the fading reaction, protein substrates appear to do so; otherwise it does not seem possible to account for the quite different course of fading upon them*. Not only is the sign of slope of the regression line changed, but there is some evidence that fading is uniformly slower on proteins than on non-proteins, though exact comparison is difficult. Very little attention appears to have been devoted to fading on this class of material, and, so far as we are aware, no suggestions have previously been made as to its nature. We have examined five possible hypotheses to account for the apparent participation of proteins in the fading reaction—

(*a*) The differences between the two classes of substrate are connected with differences between the solubility in water of the dyes examined.

(*b*) The dye molecule, excited by irradiation, transfers its energy to the protein, and in presence of air and moisture this leads to the formation of hydrogen peroxide, which thereupon oxidises the dye in a thermal reaction.

(*c*) Chemical bonds formed between protein substrate and adsorbed dye alter the reactivity of the latter.

(*d*) The observed differences are due to variation in the ratio of azo to phenylhydrazone tautomer in the dyes, as between the two classes of substrate, since it has previously been suggested [13] that variation in this ratio may account for the differences in fading rate between the individual dyes on any one substrate.

(*e*) On protein substrates the dye is faded by reduction.

These hypotheses will now be discussed more fully.

EXAMINATION OF HYPOTHESES OF FADING MECHANISM ON PROTEINS

(*a*) *Effect of Water-solubility*

This hypothesis was examined first because the only information available at the commencement of this work was to the effect that water-soluble dyes in gelatin differ in their fading from water-insoluble dyes on cellulosic substrates. It has now been shown in this work that the slope of the line (Table I) is reversed when the water-soluble (R-acid) dyes are applied to cellulose and they then resemble the insoluble class. The effect of fading water-insoluble dyes on proteins has not been determined in this work because of experimental difficulties in obtaining satisfactory coloration. All the available evidence, however, is against there being any connection between the water solubility of the dyes and their fading differences on the two classes of substrates.

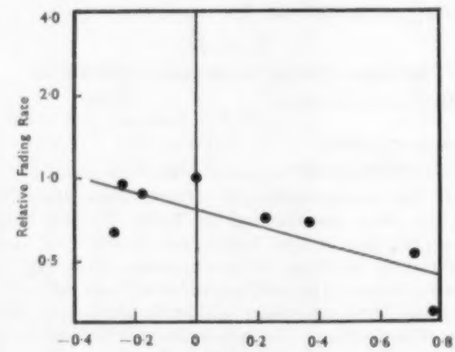


FIG. 14—Relation between Relative Oxidation Rate and σ-Value for Alkaline Hydrogen Peroxide and Gelatin

(*b*) *Possible Action of Hydrogen Peroxide*

This hypothesis was examined since at first sight it appears to offer a reasonable explanation of the observed phenomena, for the following reasons—

(i) The relative fading rates on wool or gelatin of the series of R-acid azo dyes on the one hand, and the relative rates of oxidation by hydrogen peroxide under acid conditions* on the other, are

* Except that it might be due to tautomeric changes (see below).

* In solution; the oxidation in gelatin is somewhat irregular.

influenced in the same sense by the nature of the substituent group in the dye (Fig. 9–11, 13, 14).

(ii) Further, a soluble protein, serum albumin, is reported to form hydrogen peroxide on irradiation [34] at 2500 A.; and in presence of an excited dye molecule, longer-wavelength radiation might produce a similar action in the case of protein fibres.

It was found possible to test this hypothesis readily after it had been discovered that the relative rates of oxidation by hydrogen peroxide of the R acid series of dyes on gelatin are reversed when the medium is changed from acid to alkaline in reaction; i.e. they then have the same sign of slope (Table I) (Fig. 14) as for fading on non-proteins. Therefore, if thermal oxidation by peroxide is responsible for fading on proteins, in an alkaline medium the relative fading rates of the dyes on a protein substrate should also be similar in sense to those on non-proteins.

The test experiments showed (Table III) (Fig. 11), however, that there is no significant difference in relative fading rates when irradiation is carried out under either acid, alkaline, or neutral conditions. The individual fading data are scattered, but all appear to lie about the same straight line for both silk and wool, under all three sets of conditions, and indeed the mean fastness values for each dye, for the whole series of experiments, exhibit good linearity (Fig. 11). There is quite definitely no tendency for the line to reverse its slope when the tests are made under alkaline conditions, and therefore it does not appear that hydrogen peroxide thermal oxidation can be important in fading on proteins.

TABLE III

Mean Light Fastness Grading of Aniline→R Acid Dyes on Silk and Wool

(Arclight exposures*)

Substituent in Diazo Compound	Substrate and Conditions							
	Silk			Wool				
	Acid	Neutral	Alkaline	Acid	Neutral	Alkaline	Pyruvic Acid	H_2O_2
H ...	5·0	5·2	4·4	4·5	5·0	4·3	2	4·6
m-Cl ...	4·4	4·4	4·1	4·5	4·8	3·8	1·6	4·5
p-Cl ...	5·2	4·6	4·3	4·3	4·6	4·3	1·8	–
m-NO_2 ...	4·3	4·5	3·8	4·1	4·3	4·1	1·2	4·2
p-NO_2 ...	4·5	4·8	3·4	3·8	4·1	2·5	1·1	4·1
p-CH_3 ...	5·8	5·0	4·1	4·5	4·4	5·9	–	5·0

* Gradings corrected to daylight values.

An additional test of the hypothesis was made by carrying out the light exposures in presence of pyruvic acid, a reagent for the destruction of hydrogen peroxide [22]. Again no significant difference in the relative order of fading was observed, though the absolute fading rates were increased considerably (this is discussed below). Had fading been due to peroxide, the presence of pyruvic acid would have destroyed the oxidising agent, possibly leaving the dye open to attack by the agent responsible for fading on other substrates. The relative order of fading might then have been reversed.

(c) *Influence of Bonding to the Substrate*

The principal forces binding acid dyes to protein fibres are believed to be electrovalencies, but undoubtedly other influences are operative, probably van der Waals forces and/or hydrogen bonding [37]. If the latter is effective, then it must occur between amino, peptide, etc. groups in the protein and suitable groups, in the present instance the azo group, in the dyes; and it was at first considered that the intermolecular linkage of the active group in the dye in this manner might alter the reactivity of the molecule as a whole in such a way as to account for the observed effects in fading.

To test this hypothesis, the dyes were exposed in non-protein films (carboxymethyl cellulose) to which had been added various simple compounds which contain the groups, viz. carboxyl, amino, and peptide, most abundant in proteins. Adipic acid, *N*-*n*-butylpropionamide, ethylenediamine, and nylon 66 salt were the compounds chosen. Up to the practicable limits (20–40% on the weight of cellulose ether), none of these compounds had any effect upon the relative order of fading (with the exception that the higher concentrations of nylon salt produced irregularities in relative fading rates). It does not, therefore, seem that hydrogen bonding between the dyes and the groups concerned can account for the fading phenomena on proteins.

(d) *Effect of Tautomeric Ratio*

Burawoy, Salem, and Thompson [8] compared the ratio of phenylhydrazone to hydroxyazo tautomer in a series of water-insoluble phenylazo-β-naphthol dyes in various solvents, by measuring the relative heights of the respective peaks in the absorption spectra. A similar comparison may be made of the present water-soluble dyes both in aqueous solution and in several solid films (Table IV) from the complete absorption curves shown in Fig. 15–22. (These curves are plotted with logarithmic ordinates, so that a curve for any given dye has the same shape at any concentration.) The data of Table IV are not quantitative, because the position and the height of the true maxima of the individual tautomers are unknown, and the height of the peaks observed depends on the overlap of those of the two systems. No firm conclusions can, therefore, be drawn from these values, which in any case show no clear trends, though they do not entirely rule out the possibility that the action of gelatin may be to some extent due to its effect on the tautomeric ratios.

(e) *Evidence for Reduction and Discussion of Mechanism*

If irradiated gelatin can act as a reducing agent towards dichromates, we may suppose that it can do so towards dyes, and since the present work shows that gelatin, silk, and wool behave so similarly towards at least one series of azo dyes, it seems reasonable to suggest that all azo dyes, and perhaps those of other classes also, suffer reduction when exposed to light on any protein substrate.

TABLE IV

Tautomeric Ratio in Phenylazonaphthalene Dyes

(Ratio of resultant heights of absorption peaks, hydrazone : azo)

Substituent Group (benzene nucleus)	σ-Value	Water or Aq. Cellofas A Soln.*	Cellofas A Film*	Gelatin Film*	Nylon Film*	Ethanol–Water (50 : 50)†
p-O·CH$_3$	−0·27	2·6	2·1	1·9	1·1	0·45
p-O·C$_2$H$_5$	−0·25	2·6	2·0	1·8	1·1	—
p-CH$_3$	−0·17	3·7	2·9	2·7	1·5	1·08
H	—	3·7	2·9	2·2	1·8	1·31
p-Cl	+0·23	3·5	2·8	2·2	1·0	1·26
m-Cl	+0·37	3·4	2·5	1·2	1·9	—
m-NO$_2$	+0·71	2·9	2·0	0·2	1·7	>2·0
p-NO$_2$	+0·78	3·7	2·6	0 (?)	2·5	>2·0

* Water-soluble (R acid) dyes. † Water-insoluble (β-naphthol) dyes[8].

When exposure is made in presence of pyruvic acid (Table III), there is a striking increase in the fading rate of each one of the series of dyes, but the relative order, as determined by the plot against σ-value, is unchanged. This is to be expected if the fading reaction is a reduction.

The proteins probably do not behave as hydrogen donors merely by virtue of their content of hydrocarbon groups; i.e. they do not act in the same manner as the hydrocarbon solvents are supposed to do[5,34], because both methyl ethyl cellulose and nylon, which also contain a large proportion of hydrocarbon groups, act in the opposite sense to proteins.

Photochemical excitation of the substrate itself might account for its participation in fading, but the ultraviolet absorption of gelatin and nylon rises to a high value only well below 3650 A., which is the lowest effective wavelength used in our fading tests, and at that wavelength the films of these two substances had nearly equally low absorption, so that neither is likely to be directly excited photochemically under the present conditions. It is known that wool is decomposed on exposure to sunlight and air, the cystine linkages being hydrolysed with formation of thiol and aldehyde groups and hydrogen sulphide, which is eventually oxidised to sulphur dioxide and sulphuric acid[33]. This could account for reduction of dyes on irradiation on wool*, but not on silk, which has no cystine linkages; gelatin also has very few.

It has been shown above that none of the groups—carboxyl, amino, and peptide—appears to be responsible for the fading characteristics of proteins; this conclusion was based on tests made by adding monomeric compounds to the substrate. There might still be the possibility that the presence of these groups as integral parts of the substrate molecules would give a different result, but the fact that both nylon and polyglycine behave as non-proteins shows that this cannot be so. Therefore, if proteins do exert a chemical influence on fading, they probably do not do so by virtue of any property inherent in their main molecular chains. The influence appears therefore to arise in some property of the side-chains in proteins. This is as much as can be said on the basis of the present results.

In this connection, however, significance may be attached to an investigation by Carter[9], who examined the photo-oxidation of a number of organic compounds in solution in water or alcohol, in presence of a fluorescent compound, e.g. porphyrin, haematoporphyrin, Methylene Blue, or Eosin, acting as sensitiser. In these circumstances, only aromatic compounds containing hydroxy or amino groups were found to be reactive, and included amongst these were two constituents of the proteins of wool, silk, and gelatin, viz. histidine and tyrosine; tryptophan, which occurs in wool[36], was also effective. Other types of aromatic compound and all aliphatic compounds were inactive. No hydrogen peroxide was formed during the reaction. In this type of reaction the sensitiser presumably suffers reduction, so that there is a parallel with the dye–protein fading systems, and it may be that the effect of protein substrates on fading is in some way attributable to their histidine or tyrosine content.

* It is reported[6], however, that many azo dyes on wool exert a protective effect towards degradation in (arc)light.

NATURE OF INITIAL ATTACK ON DYE MOLECULE

It has already been suggested that the azo group must suffer the initial attack in azo dye fading[3,13,24,28], and the present work serves to confirm this. Desai and Giles[13] supposed that the phenylhydrazone form may be the most susceptible tautomer, and the azo form the least, but the evidence of Burawoy *et al.*[8] suggests that the reverse may actually be the case. No further evidence is yet available on this point. The azo group has a slight degree of water attraction[18], probably owing to its hydrogen-bonding power. It is therefore in close enough contact with adsorbed water in the fibre to react directly therewith when the molecule is excited, and to add a hydroxyl radical in the way suggested by Hillson and Rideal[24]. There is no evidence in the present work that the presence of the highly water-attracting sulpho group has any consistent accelerating effect on fading. The degree of water-solubility of azo dyes is therefore not directly a rate-determining step in fading. It may be so, indirectly, in affecting the physical nature of the dye in the dried fibre and hence the surface area exposed to air.

Light Absorption Curves for Phenylazo-R Acid Dyes

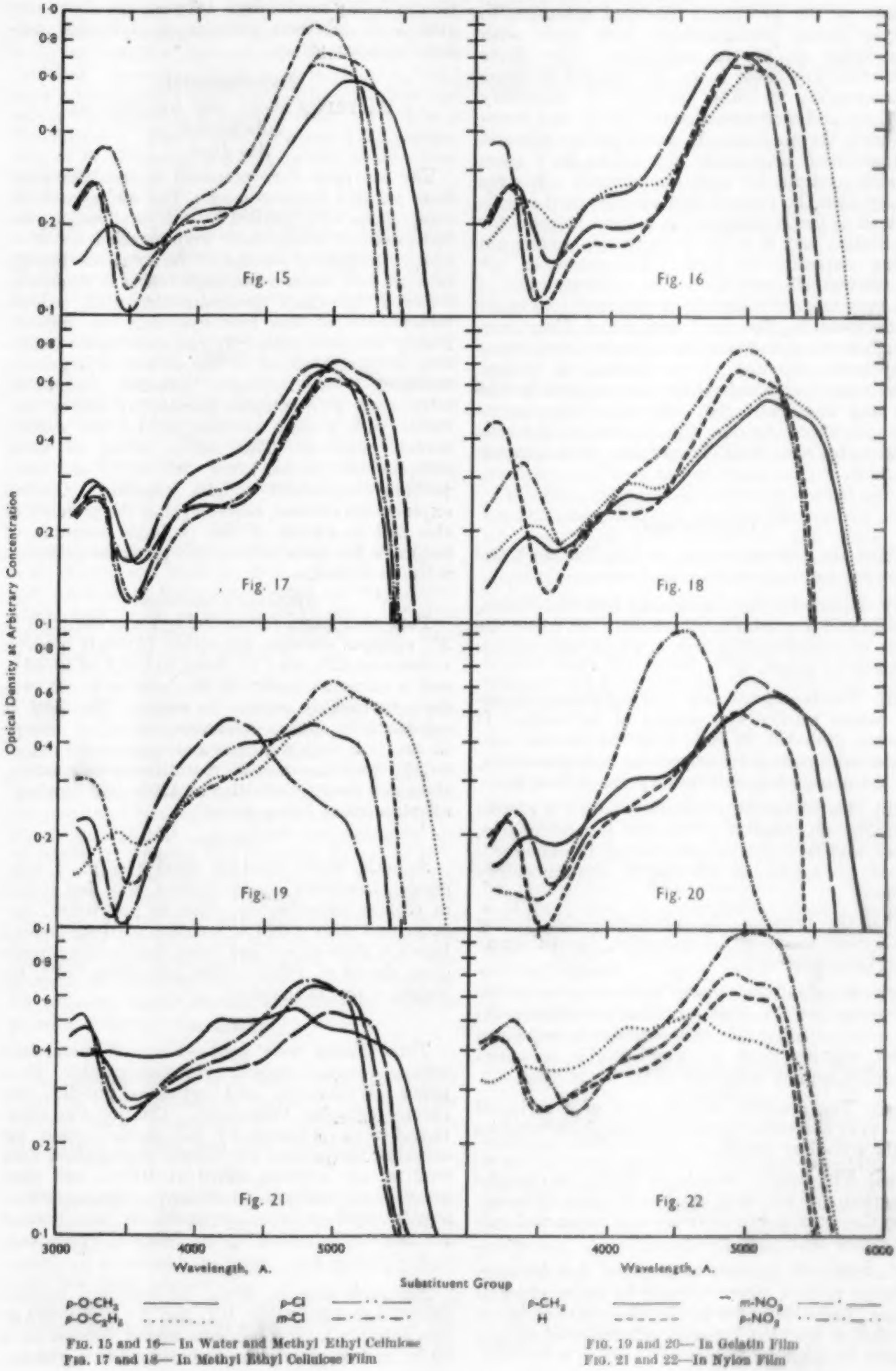


FIG. 15 and 16— In Water and Methyl Ethyl Cellulose
FIG. 17 and 18— In Methyl Ethyl Cellulose Film

FIG. 19 and 20— In Gelatin Film
FIG. 21 and 22—In Nylon Film

ATTEMPTED DETECTION OF FADING PRODUCTS

Most of the previously reported attempts to analyse fading products have been made with dyes faded on fibrous substrates. The fibres themselves are liable to be decomposed in these circumstances, in either primary or secondary reactions, and their breakdown products may interfere with the analysis. It was therefore thought that anodised aluminium film might be a more suitable medium for such experiments. It dyes readily with the type of acid azo dye used in this work, it is easily prepared in a form suitable for irradiation, and it is likely to remain unaffected during exposure to light. Unfortunately, no success was achieved by its use. No products of any type whatever (except unchanged dye) could be detected in the dyed and faded film, even though it was found possible to detect the types of compounds expected to be formed, in control experiments, in which they were applied to the film and then extracted. We can only suppose that decomposition on this substrate proceeds rapidly to the final breakdown into gaseous products.

Conclusions

From the present results and earlier work the following conclusions may be drawn—

(i) Substrates may be divided into two classes, protein and non-protein respectively, on which the effect of substituent groups in simple azo dyes is opposite in sense.

(ii) The fading reaction is of a different chemical nature on the two classes of substrate. It appears probable, in fact, that the protein substrates take part chemically in the fading reaction, but the non-protein substrates perhaps do not.

(iii) On non-protein materials fading is almost certainly an oxidation process involving dye, water, and probably oxygen, though in some cases specific groups in the dye may be simultaneously reduced.

(iv) On proteins the most probable fading mechanism seems to be reductive, the substrate itself being involved.

(v) A substituent group *meta* or *para* to the azo group has the same quantitative influence on the relative fading rate of an azo dye in any given series, whether these are water-soluble or water-insoluble, on any substrate of the same class.

(vi) The absolute fading rates of a series of dyes vary according to the physical characteristics of the dye–fibre system.

(vii) The initial attack in fading is on the azo group and probably involves transfer of energy from the excited dye molecule to a water molecule associated with that group.

Variation of fastness of a given dye between different protein substrates may be due to physical causes, but differences in the chemical nature of the fading reaction between substrates obviously cannot be ruled out here.

So far no evidence is available that the distinction in fading mechanisms between the above two classes of substrate extends to dyes not containing an azo group.

Experimental

MATERIALS USED AND METHODS OF COLORATION

Azo Dyes

The azo dyes were prepared in the laboratory from purified intermediates. The water-insoluble compounds were purified by recrystallisation; the water-soluble compounds were purified to 95·5–100% strength by passage of the solutions through cationic and anionic exchange resins in sequence, followed by exact neutralisation with sodium bicarbonate of the free dye acid so formed. Purity was determined by the dichromate oxidation method [1b]. Some of the earlier experiments, including some hydrogen peroxide oxidations, were made with samples purified by salting out, either with sodium chloride or by the sodium acetate method. The purity values of these samples were rather lower (90–100%) and they probably contained sodium chloride. Control experiments showed, however, that the presence of this salt in excess of the probable amounts of impurity has no effect on the peroxide oxidation rates measured.

Anodised Aluminium

Pure aluminium foil (0·002 in.) was anodised in 3% aqueous chromic anhydride (AnalaR quality) solution at 45°c. for 1 hr. using an e.m.f. of 40–45 v. and a current density of 10 amp./sq.ft. It was then thoroughly rinsed in water. The film is substantially pure γ-alumina (Al_2O_3). Strips (5 cm. × 5 cm.) were cut and dyed in 50 c.c. of 0·02% dye solution at 60°c. until near exhaustion, then well rinsed, and dried at 120°c., no "sealing" aftertreatment being given.

Asbestos

Smooth, white asbestos sheet (1·2 g., 1 mm. gauge), free from organic matter, was first rinsed in carbon tetrachloride, then in hot water, impregnated with a 0·01 M. solution of dye, pressed between filter paper, and dried thus between plate glass sheets at 100°c. This left about 0·3% by weight of dye in the sheet.

Cellulose

Three forms were used—bleached mercerised cotton sateen, smooth chromatographic filter paper (Whatman), and cellulose powder (for chromatography, Whatman). The first two mentioned were coloured by the method used for asbestos; the powder was simply impregnated with 0·02 M. dye solution, dried at 100°c., and then ground to a uniform consistency. The naphthoic arylide dyeings were prepared in the normal manner on the cotton sateen, followed by soaping.

Collodion

For each sample, 8 c.c. of collodion varnish (Necol Label Adhesive, ICI) and 2 c.c. of 0·008 M. dye solution in acetone were mixed, spread on a 2½ in. × 4 in. glass plate, and allowed to dry in air.

Gelatin

A 6% aqueous solution (14 c.c.) of gelatin, of pure "inert" photographic quality, was mixed with 9 c.c. of 0·0005 M. dye solution and poured on a "subbed" photographic glass plate (4 in. × 5 in.) on a screw-levelled platform. When the film had set, it was placed in a steady stream of air from a fan until dry. This procedure ensured the production of films having uniform optical density over their whole area.

Methyl Ethyl Cellulose

A 4% aqueous solution of Cellofas A (ICI) was prepared in the cold by stirring continuously for 24 hr., and then centrifuging at 2,500 r.p.m. for 1 hr. in four 250-c.c. containers, to deposit fibrous material. The supernatant liquor was then used for film casting, 17-c.c. portions being mixed with 9-c.c. portions of 0·0005 M. dye solutions and poured on glass plates as for gelatin. The plates were levelled on a sheet of plate glass, placed on a metal surface heated from below by four 100-w. tungsten lamps. This procedure gave the most uniform films, but even so, inequalities were noticed round the edges, and only the central parts were used.

Nylon

Transparent 0·003-in. nylon film, in 2·5 in. × 4 in. strips, was dyed in 400 c.c. of 5×10^{-6} M. dye solution at 95°c. for 90 min., a little dilute acetic acid being added after 45 min. to effect complete exhaustion. The material was then well rinsed, and dried at 100°c.

Polyglycine

The only suitable solvent for this material was found to be dichloroacetic acid, but it was not possible to make satisfactory films from the solutions, because the gel cracked and broke up on drying. The material had therefore to be used in the powdered form as follows— 0·5 g. was dyed at a liquor ratio of 100 : 1 in a bath containing 20 c.c. of 0·0005 M. aqueous dye solution, 10 c.c. of 10% sodium sulphate solution, and 1·5 c.c. of 1% aqueous sulphuric acid solution. The bath was raised to the boil in 30 min., and dyeing continued at the boil for 1 hr., the liquors being then substantially exhausted. The dyed powder was filtered off, washed with water, and mounted for exposure in the manner described for cellulose powder (below).

Silk

One-gram portions of boiled-off silk fabric were dyed to near exhaustion in 0·2%* depths from 100-vol. baths containing 1% sulphuric acid, on the weight of fibre, and then rinsed and dried.

Tile

Unglazed tiles (free from water-soluble material) were smoothed with fine emery paper, dusted clean, impregnated with 0·5 M. solutions of dye, by means of a camel-hair brush, and then air-dried until free from solvent.

An attempt was made to cast blocks of plaster of Paris containing aqueous solutions of dye, but the results were unsatisfactory because of concentration of dye at the surface during drying.

Wool

One-gram patterns of scoured worsted flannel were dyed by the method used for silk.

Other Substrates

Other materials used unsuccessfully in forming films were— sodium carboxymethyl cellulose (Cellofas B, ICI), solutions of which proved too viscous; and polymethyl methacrylate (ammonium salt) and polyvinyl alcohol, both of which failed to give coherent films.

MOUNTING OF COLOURED SUBSTRATES

Aluminium, asbestos, cotton, and paper samples were cut into 5 cm. × 1 cm. strips, and stapled to card with a hinged black card flap covering one-half of the surface.

Cellulose powder was packed into 5 cm. × 1 cm. rectangular apertures cut into thick card and sandwiched between glass plates, which were then firmly bound with tape. One half of each pattern was protected by a hinged black card.

The films from gelatin and methyl ethyl cellulose were treated as follows— A strip (50 mm. × 11 mm.) was cut from the centre of the plate, the film surface was covered with a second, equal-sized portion of similar glass, and the ends were bound together by tape to prevent peeling. This size of strip is suitable for direct insertion in the spectrophotometer. For the experiments using filtered light, the cover glass was the filter itself (Chance OX1, 2 mm. thick), which was placed towards the lamp.

INSOLUBLE DYES IN GELATIN

Attempts to prepare samples of gelatin or wool satisfactorily coloured with insoluble azo dyes were unsuccessful. If coupling was carried out *in situ* in gelatin, the dye crystallised out irregularly on standing; whereas on wool some coupling with the fibre substance itself occurred. Application to wool by impregnation with solutions in glacial acetic acid gave very irregular fading results, possibly because of the formation of bulky crystals in the fibre. It was considered undesirable to use dispersing agents to give more even coloration, because this would further complicate the system. Experiments with this class of dye on proteins were therefore abandoned.

HYDROGEN PEROXIDE OXIDATION TESTS

In Solution

Portions (2 c.c.) of dye solution ($2 \cdot 21 \times 10^{-4}$ M.) were buffered, diluted to 20 c.c. after addition of 2 c.c. of 30% (wt./vol.) hydrogen peroxide (prepared from 98% "high test" H_2O_2), and kept in a 25°c. thermostat in the dark, in ground-glass or rubber stoppered test tubes. Agitation was not employed, as it tended to make the results inconsistent. Small quantities of the liquid were removed at intervals for optical density measurement in a photoelectric absorptiometer.

The experiments were continued up to 6 hr. for alkaline and neutral solutions, and 40 hr. for acid

* Adjusted in each case to give equimolar quantities.

solutions, in which oxidation rates were lower. Before measurement of the samples from the alkaline peroxide solutions, they were diluted with an equal volume of 0·05 N. hydrochloric acid to prevent the formation of oxygen bubbles on the surface of the cell.

Fig. 13 shows the rates of change of optical density of the various solutions at three pH values, and in Fig. 14 the rates of decomposition relative to the unsubstituted dye are shown plotted against the σ-value. The change of sign of the slope of the curves so obtained with change in pH value is very marked.

On Gelatin Film

Portions of coloured film prepared as already described (but uncovered) were placed in a Perspex (ICI) cage and allowed to stand in a desiccator, in the dark, over mixtures of 5 c.c. of 95% ("high test") hydrogen peroxide and 5 c.c. of ammonia solution (sp. gr. 0·880) or glacial acetic acid respectively. (The films were exposed in this manner to the alkali or acid alone, for two days before the peroxide was introduced.) The films were removed at suitable intervals for optical density measurement in the spectrophotometer, and the vessel was recharged with fresh reaction liquor each time. The relative fading rates were plotted against σ-values as described below for irradiation tests.

FADING TESTS FOR COMPARISON WITH PEROXIDE OXIDATION

The exposures of wool and silk at different pH values and in pyruvic acid and hydrogen peroxide vapours were made by hanging the samples in corked test tubes, at equal distances from the arc, over 1–10% aqueous solutions of glacial acetic acid, water, ammonia (sp. gr. 0·880), hydrogen peroxide, or pyruvic acid, the patterns having previously been steeped overnight in the respective liquids. The experiments were run in triplicate and the relative positions of the tubes were frequently changed, in a random manner, during exposure.

ILLUMINANTS

Most of the irradiation tests were made with mercury-vapour light, but some were made by daylight or enclosed carbon arclight. Details are as follows—

Daylight

Exposure was made through glass to skylight with a southern aspect. Fading rates were determined by means of the *B.S.* 1006 standards [7], as described on p. 499.

Arclight

A 250-v. D.C. carbon arc enclosed in Pyrex glass was used, patterns being exposed at 9 in. from the arc against the inner wall of a glass cylinder, with free upward circulation of air (air temperature ca. 40°c.)*. Fading rates were determined by means of the *B.S.* 1006 standards [7]. Frequent random changes of position of patterns and standards were made.

Mercury-vapour Light

Osira lamps (General Electric) of both 250 w. and 400 w. capacity were used, run directly from the mains supply with appropriate chokes. A constant-voltage transformer was tested, but it was found to reduce the illumination by as much as 90% and its use was therefore abandoned. Cylinders of sheet aluminium, 17 in. in diameter × 15 in. high, centred on the lamps, with an internal annular shelf for the samples, opposite the mid-point of the arc, were used, with free ventilation space. The relative fading rates were found to be identical in the two lamps (250 w. and 400 w. respectively) with or without the use of the transformer. These lamps have a weak continuous spectrum as a background with a number of superimposed strong monochromatic bands (Fig. 23).

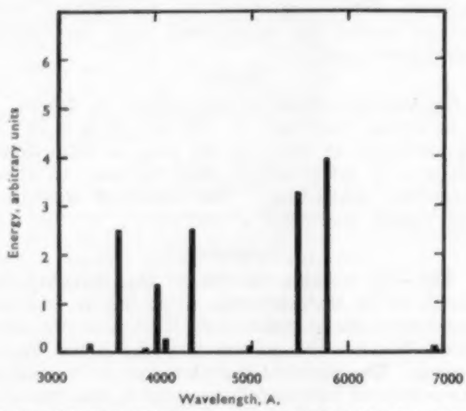


FIG. 23—Energy Distribution Curve of Osira (G.E.C.) 400-w. Lamp. A small amount of continuous radiation (too small to appear on this scale) occurs throughout the spectrum

TEMPERATURE MEASUREMENTS, ETC.

By embedding thermocouples in gelatin films, as used in the fading experiments, the internal temperatures were recorded, both for uncoloured film and for film coloured with a high concentration of an R-acid dye (much higher than any used for fading tests), and compared with the surrounding air temperature (Table V).

TABLE VI

Irradiation Temperatures (°C.)

Substrate	Mercury-vapour Lamp 250 w.	400 w.
Air	41	56
Gelatin film ...	40	65
Dyed gelatin film	52	67–70

Apart from the exception noted, all the temperatures remained steady within ± 1°c. throughout each fading test, though the gelatin films required about 1 hr. from the start to reach the maximum temperature.

* Published information confirms that temperature change has little effect on fading rate, at least below about 60°c. (air temperature [38]). Changes in humidity have considerable effect on the fading rate of many dyes [38], but the relative humidity of the atmosphere surrounding the patterns appeared to remain steady at ca. 30% in the present tests (arclight) as determined by hair hygrometer.

Films left exposed to the lamp for two days had moisture contents as follows— 250-w. lamp, gelatin 12·0%, Cellophane 5·6%; 400-w. lamp, gelatin 2·8%.

CHOICE OF WAVEBAND FOR FADING EXPERIMENTS

In all such fading experiments the problem arises of correctly comparing the fading rates of dyes which have different spectral absorptions and are illuminated by light which is never uniform in energy distribution. Atherton *et al.*[2, 3] adopted a method of determining the integrated product of the energy absorption of each dye and the energy output of the lamp, both determined over the whole spectrum. It is, however, doubtful whether this procedure is justified, since no account is taken of the relative quantum efficiencies in fading of the different regions of the spectrum. Very little is yet known about these efficiencies, but it has been found that with some dyes the efficiency is very high in the near ultraviolet and falls rapidly to zero near the centre of the visible spectrum[11]. If this were so with the present series of dyes, then (*a*) the integration procedure would be likely to decrease the reliability of the results, and in fact it does have the effect of increasing the irregularity of the data (Fig. 7); and (*b*) the use of the unfiltered mercury-vapour light, having predominant energy output in the region of greatest fading efficiency, should give reliable results with a series of dyes which, like the present ones, are of closely similar spectral absorption characteristics in that region*.

An experiment was therefore carried out in which two identical series of the R-acid dyes in methyl ethyl cellulose film were compared for fading rate (*a*) in the unfiltered light of the lamp, and (*b*) in filtered light of λ 3650 A. The results (Fig. 6) show no significant difference between the effects of the two methods of illumination. In subsequent experiments with the ultraviolet lamps, therefore, unfiltered light was used.

COMPUTATION OF RELATIVE FADING RATES

In Daylight or Arclight

The use of the *B.S.* 1006 standards has enabled a simple method of computation of the fading rates of related dyes in variable light to be worked out †. A sample is considered to have faded when a just perceptible loss of depth is evident to the eye ‡, and it is then graded by the *B.S.* 1006 standard which, under the same exposure, shows a similar loss. An approximate estimate of grading intermediate between individual standards, when necessary, was made (in arclight) by interpolation on a logarithmic scale by noting the time at which the fade appeared, compared with that required to fade the standards immediately above and below.

It is then assumed that the observed loss of depth represents in each case, to a first approximation, the destruction of the same fraction α of total dye. The *B.S.* 1006 standards between 1 and 6 inclusive have been shown by Ricketts[33] to be uniformly spaced, each one fading at twice the rate of that next above*. (In our tests no sample with fastness above Grade 6 has been used.)

The proportion α of dye faded is thus destroyed in a time tf^{n-1} or $(t/f)f^n$, where t is the time required for Standard No. 1 to fade, f is the factor by which the standards are spaced, and n is the rating (grade number) of the sample. It thus follows that in time t the proportion of the original dye destroyed is $f\alpha/f^n$†, which is therefore a measure of the fading reaction rate of the dye concerned. This reaction rate may thus be expressed as $kf\alpha/f^n$, where k is a constant, and it is clearly inversely proportional to the antilogarithm of the grade number, and independent of the spacing factor of the standards, provided that fading is judged throughout on the same basis. Hence if the grade numbers of a substituted dye and the corresponding unsubstituted compound are respectively n and n_0, the ratio of their rates of destruction is $n_0 - n$. By plotting $n_0 - n$ against σ-value for a related series of dyes, the effect of substituents upon fading rate can thus be determined. Fig. 10–12 show the results of this treatment of a number of light exposure tests. Data from single samples are scattered, but the observation of several replicates of each sample leads to a much improved linear relation showing definite influence of structure upon fastness.

The general agreement with spectrophotometric results serves to justify the underlying assumption on which the visual assessments were made. In Fig. 12 (see column (vii), Table VI) there are plotted also some data from a manufacturer's publication[35] giving the light fastness of various insoluble azo dyes from arylides of 2:3-hydroxynaphthoic acid (Brenthols). These all refer to bases derived from *o*-toluidine and not aniline, and as no data for *o*-toluidine itself for use as standard are available, those for aniline (column i) are used instead. (From the data of Atherton and Peters[2] it appears that these two bases differ hardly at all in their effects on fading rate.) These data, again, agree closely with the present results on all non-protein substrates.

Gradings in arclight were converted to the corresponding gradings in daylight, before plotting, by use of the regression line of sunlight assessment on Fadeometer assessment given by Morton[29]. The data of Tables III and VI can be considered only approximate, and the figures to the right of decimal points are not considered individually very significant, though it should be pointed out that

* For the above reasons, dyes of similar hue but different chemical classes, which may thus differ widely in ultraviolet absorption characteristics, cannot be reliably compared by exposure to this type of lamp, and indeed the *B.S.* 1006 standards fade in quite irregular order when exposed to it.

† Cf. Desai and Giles[14], but the ordinates should read 1, 0, −1, −2 (down) and not as shown. The anomalous position of the methoxy substituent shown is now believed to have been due to unsuspected impurities in one of the dye samples.

‡ Morton[29] considers that "the fastness of a dyeing should be assessed at the smallest depth of fade (change in appearance) which is commercially significant".

* At least for six "just perceptible" steps; for three such steps the factor rises from 2·0 to 2·2.

† Assuming, to a first approximation, that the time-loss of dye relationship is linear over the short fading ranges studied.

TABLE VI

Mean Light-fastness Grading of Water-soluble and Water-insoluble *o*-Hydroxyazo Dyes on Opaque Substrates

(Daylight and arclight* exposures)

Substituent in Diazo Cpd.	σ-Value	Substrate and Coupling Component i	ii†	iii	iv	v	vi	vii	Grand Mean (i–v)
H (control)	—	3·9	1·7(a)	4·3	2·8	1·5	4·8	(3·9)	2·8
m-Cl	+0·37	4·6	2·0(a)	5·0	3·3	1·2	—	4·6	3·2
p-Cl	+0·23	4·4	1·3(a)	4·5	4·3	2·2	—	4·5	3·3
m-NO_2	+0·71	4·8	2·7(t)	5·5	3·3	2·3	—	4·7	3·7
p-NO_2	+0·78	4·8	2·8(p)	5·5	4·3	4·3	—	5·2	4·3
m-CH_3	−0·07	—	—	—	3·8*	1·6*	—	—	2·7
p-CH_3	−0·17	4·0	2·7(t)	2·8	3·0*	2·0*	—	—	2·9

i = Anilide, *o*-anisidide, and *o*-toluidide of 2:3-hydroxynaphthoic acid. Mean grading for three dyeings of each arylide, on cotton.
ii = β-Naphthol; paper.
iii = β-Naphthol; tile.
iv = 2-Naphthol-3:6-disulphonic acid (R acid); paper.
v = 2-Naphthol-3:6-disulphonic acid (R acid); tile.
vi = 2-Naphthol-3:6-disulphonic acid (R acid); wool.
vii = Mean values for Brenthol dyeings on cotton; 17, 18, 18, 15 combinations respectively; 1–1·5% Brenthol on fibre; gradings between 1 and 6.

* Arclight figures corrected to daylight values. † Solvents— (a) = glacial acetic acid; (p) = pyridine; (t) = toluene.

they were each obtained by averaging several assessments estimated to the nearest half-grade number or closer. Those in column (vii) (Table VI) are more significant, even though the differences are smaller, because they are the means of larger numbers of assessments.

In Mercury-vapour Light

For opaque substrates the time of exposure required to produce just perceptible loss of depth was noted for each sample, and the logarithm of the ratio of the fading rates of substituted dye and unsubstituted dye was plotted against the corresponding σ-value.

Fading in the transparent films was determined spectrophotometrically with a Unicam SP 500 photoelectric spectrophotometer. The complete light absorption curve for each dye between 3000 and 7000 A. was first measured (e.g. Fig. 15–22), and the rate of fading was determined by noting the value of the optical density at the peak absorption wavelength, at intervals during the irradiation period. A typical series of fading-rate curves is shown in Fig. 24. It will be observed that in many cases the curves are irregular during the early stages of fading; often the optical density at first increases a little before decreasing. No change in the overall shape of the light absorption curves could be detected in the course of these irregularities, and it is assumed that they are due to purely physical changes, perhaps to some form of rearrangement of dye particles occasioned by some loss of moisture in the film. Changes of this sort may perhaps account for the well known irregularities often noticed in practice in the early stages of fading of some dyed fabrics when under test for light fastness.

The relative fading rate–substituent relationship was determined by noting the time t required for a 10% loss of depth of colour for each dye after a chosen time at which all the films in the set had settled down to a steady rate of fade (see Fig. 24), and then plotting log t_0/t, where t_0 is the corresponding time for the unsubstituted dye, against σ-value.

Throughout the work, the dyes were exposed in complete sets (i.e. sets containing examples of each substituent group) at a time.

NOTE ON σ-VALUES

Some σ-values may vary according to the type of compound containing the substituent. Thus, Hammett [20] quotes two values for the *p*-nitro group, one (+ 1·27) for derivatives of aniline and phenol and the other (+ 0·778) for the reactions of all other compounds. The second value fits most of the present fading data better than the first, and has consequently been used in this paper, though the first value was used in plotting a small proportion of these data in an earlier note [14].

DATA PLOTTED

The fading data shown are the mean values of two or three individual tests, except the commercial data included in Fig. 12, where more than 15 assessments are represented, and those in Fig. 5,

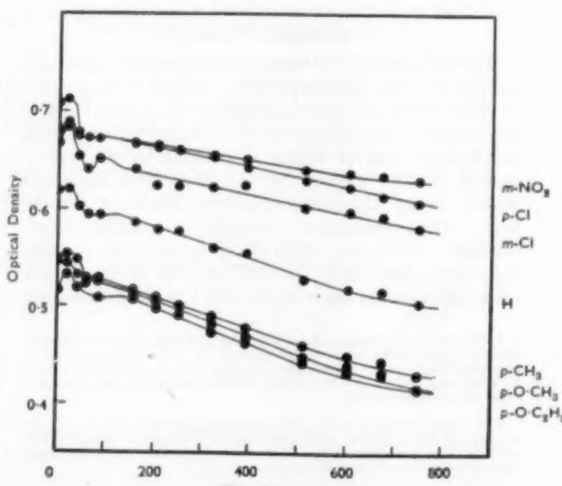


FIG. 24— Typical Fading Rate Curves (Phenylazo-R Acid Dyes on Nylon Film)

which are single values. The best straight lines, determined by the least-squares method where necessary, are shown. Strictly, these lines should be determined from each individual point. It was found that virtually the same results could be obtained by the much less laborious process of taking the lines from the mean points shown.

EXAMINATION OF FADED ANODISED ALUMINIUM

The following dyes were used— Orange I (*C.I.* 150), Orange II (*C.I.* 151), aniline→R acid (*C.I.* 28), *p*-toluidine→R acid (*C.I.* 64), and aniline→α-naphthol. These were chosen because of their relatively simple structures and the possibility they offered of indentification of unsulphonated decomposition products from both first and second components.

Partition chromatography on filter paper strips (16 cm. × 2 cm.), using *n*-butyl alcohol saturated with water as the moving phase, was used, as already described[13] to identify the products of ceric sulphate oxidation of these dyes. In every case a diazonium compound was detected at the upper end of the strip (nearest the source) after about 6 hr. development, and a quinone at the further end. If the reaction mixture was previously boiled, a phenol was detected at the upper end and (by the fluorescein fusion test) phthalic acid (except in liquors from the R-acid dyes) at the bottom.

Pieces of pure aluminium foil (6 in. × 6 in.), anodised in sulphuric acid, were dyed and exposed to the light of an enclosed arc for one week, when nearly all the dyes showed considerable fading. The faded foil samples were then Soxhlet-extracted with either water, ethanol, benzene, toluene, or pyridine, or they were warmed with a 50% aqueous solution of concentrated hydrochloric acid, after which the extracts were evaporated to small volume on the water bath, and were tested by partition chromatography. Unfaded dye was present, but in no case could any trace be detected of any of the expected oxidation products. Yet, in control experiments, it was found possible to detect such products when known samples were applied to the foil and later Soxhlet-extracted. It must be assumed that the products are so completely oxidised that no traces of the first products remain. It should, however, be remarked that negative results were similarly obtained in experiments on filter paper faded after impregnation with a solution of each of these dyes, respectively, whereas Haller and Ziersch[19] were able to detect oxidation products from (much larger) faded patterns dyed with similar phenylazo-β-naphthol dyes.

* * *

One of the authors (H.R.C.) is indebted to the International Wool Secretariat, one (N.F.D.) to the Government of India, and one (N.M.) to Messrs. Ilford Ltd., for financial assistance.

We also wish to record our thanks to Dr. (late Professor) W. M. Cumming and Professor P. D. Ritchie for their continued interest and encouragement, to Mr. R. B. Collins and Dr. W. Good for helpful discussions, and to Mr. G. Baxter for the work recorded in Fig. 5 and Table V.

Thanks are due also to Messrs. Imperial Chemical Industries Ltd. (Dyestuffs Division, Nobel Division, Paints Division, and Plastics Division) and Ilford Ltd. for the gift of some intermediates, dyes, and substrate materials. The sample of polyglycine was supplied by Mr. H. W. Wood and Ilford Ltd. Some of the fading tests were made by courtesy of Messrs. J. & P. Coats Ltd.; and Miss I. M. Jamieson carried out the irradiation and extraction experiments upon anodised aluminium. Fig. 23 is reproduced by courtesy of the General Electric Co. Ltd., Wembley.

COLOUR CHEMISTRY RESEARCH LABORATORY
DEPARTMENT OF TECHNICAL CHEMISTRY
ROYAL TECHNICAL COLLEGE
GLASGOW C.1

(*Received 19th October 1953*)

References

1a Allingham, Giles, and Neustädter, *Faraday Soc. Discussions*, (16), 92 (1954).
1b Arshid, Desai, Giles, and McLintock, J.S.D.C., **69**, 11 (1953).
2 Atherton and Peters, *ibid.*, **68**, 64 (1952).
3 Atherton and Seltzer, *ibid.*, **65**, 629 (1949).
4 Biltz and Eggert, *Veröffentl. wiss. Zentral-Lab. phot. Abt. Agfa*, **3**, 294 (1933).
5 Blaisdell, J.S.D.C., **65**, 618 (1949).
6 Breare, *ibid.*, **65**, 693 (1949).
7 *B.S.* 1006: 1953 (London: British Standards Institution).
8 Burawoy, Salem, and Thompson, *J.C.S.*, 4793 (1952).
9 Carter, *Biochem J.*, **22**, 575 (1928).
10 Cartwright and Murrell, *Nature*, **132**, 603 (1933).
11 Collins, *Private communication*.
12 Couper, *Text. Research J.*, **21**, 720 (1951).
13 Desai and Giles, J.S.D.C., **65**, 639 (1949).
14 Desai and Giles, *ibid.*, **67**, 376 (1951).
15 Eder, *Inland Printer*, **75**, 594, 772; **76**, 91 (1925).
16 Elöd and Berczeli, *Kolloid-Z.*, **74**, 305 (1936); **75**, 66, 202 (1936);
Elöd and Schachowskoy, *ibid.*, **72**, 67 (1935).
17 Gebhard, *Farben-Ztg.*, **21**, 253: through *Chem. Abs.*, **5**, 1517 (1911); *J. prakt. Chem.*, **84**, 561: through *Chem. Abs.*, **6**, 983 (1912); *Z. angew. Chem.*, **23**, 820; **26**, 79: through *Chem. Abs.*, **6**, 155 (1912); **7**, 1613 (1913); J.S.D.C., **34**, 74 (1918).
18 Giles and Neustädter, *J.C.S.*, 918 (1952).
19 Haller and Ziersch, *Melliand Textilber.*, **10**, 951 (1929); *Z. angew. Chem.*, **43**, 209 (1930).
20 Hammett, *Physical Organic Chemistry* (New York and London: McGraw-Hill Book Co., 1940), Chapter VII.
21 Harrison, J.S.D.C., **28**, 225 (1912); **30**, 206 (1914).
22 Hartree and Keilin, *Biochem. J.*, **39**, 293 (1945).
23 Hibbert, J.S.D.C., **43**, 292 (1927).
24 Hillson and Rideal, *Proc. Roy. Soc.*, **A 216**, 458 (1953).
25 Imperial Chemical Industries Ltd., Dyestuffs Division, *The Dyeing of Cotton with Brenthol Dyestuffs*, Code No. 362/53/1051. No date.
26 Kienle, Stearns, and van der Meulen, *J. Physical Chem.*, **50**, 363 (1946).
27 Lazarev, *Z. physikal. Chem.*, **98**, 94 (1921).
28 Lead, J.S.D.C., **65**, 723 (1949).
29 Morton, *ibid.*, **65**, 597 (1949).
30 Mounier, *T.I.B.A.*, **9**, 5, 121, 237, 353, 469, 585, 587 (1931).
31 Pinte and Millett, *Bull. Inst. text. France*, (9), 29 (1949).
32 Race, Rowe, Speakman, and Vickerstaff, J.S.D.C., **54**, 141 (1938).
33 Ricketts, *ibid.*, **68**, 200 (1952).
34 Roberts, *ibid.*, **65**, 699 (1949).
35 Seyewitz and Mounier, *Bull. Soc. chim. Belg.*, **43**, 648 (1928).
36 Traill, J.S.D.C., **67**, 257 (1951).
37 Vickerstaff, *ibid.*, **69**, 279 (1953).

Some Observations on the Histology of Keratin Fibres

B. MANOGUE, M. S. MOSS, AND R. L. ELLIOTT

Sections of several different wool and hair fibres have been given chemical treatments alleged to isolate the "subcuticle membrane". The residues consist of parts of the cuticle, cortex, and medulla. The cortex residue is made up of cortical cell nuclei, fibrils, and thin membranes located at the boundaries of the cortical cells. These membranes are more resistant to treatment with sodium hydroxide solution and sodium sulphide solution than the major part of the cells, but are dissolved by proteolytic enzymes. The membranes are probably the material hitherto termed "intercellular cement".

Introduction

The classical optical microscope investigations carried out in the late nineteenth century[1–3] showed that wool and hair fibres are composed of three kinds of cell, viz. the cuticle or scale cells, which surround the whole fibre; the cortical cells, which constitute the cortex or main body of the fibre; and in the coarser fibres a central canal of air-filled cells comprising the medulla. Later workers have confirmed these findings, and the structure of the different cells has been further examined.

It has been suggested that the cells may be held together by an intercellular cementing substance[4]. Besides the component cells and the possible cementing substance, a further histological component is said to exist, the so-called "subcuticle membrane". This "subcuticle membrane" is postulated as a layer lying below the cuticle of the fibre and enclosing the cortex as a whole. In support of this, a layer which differs from the cuticle in staining properties, and which surrounds the cortex, has been observed on fibre-sections[5,6]. Several workers (Lehmann, Alexander, Zahn) have claimed that they have isolated this layer by chemical methods. Two such treatments employed were— (*a*) extraction of peracetic acid-oxidised fibre with ammonium hydroxide, and (*b*) treatment of fibres with sodium hydroxide solution[7–11]. More than 90% of the fibre was reported to be dissolved in each case, and the insoluble fraction has been identified with the "subcuticle membrane", although, in our view, no conclusive evidence has been adduced to show the actual site in the fibre of the insoluble material obtained.

The present authors and others have previously found the insoluble fraction obtained from wool fibres, after treatment with peracetic acid and ammonium hydroxide, to be heterogeneous, and to consist of parts of the cuticle, cortex, and medulla[12,13].

In this paper evidence is presented, obtained from the optical and electron microscopic examination of treated longitudinal and transverse sections, that it is not the "subcuticle membrane" which is isolated by these treatments. The investigations have revealed, however, that the residues contain very thin membranes, which were originally located at the boundaries of each cortical cell[14].

Experimental

The two treatments which were used to separate and show the place of origin of the residues were— (*a*) treatment of fibres with 1·6% aqueous peracetic acid, drying, embedding, and sectioning, followed by extraction of the sections with 0·1 N. ammonium hydroxide solution; and (*b*) treatment of sections of untreated fibres with 2 N. sodium hydroxide solution at 60°C. for 7 min.

TREATMENT OF FIBRES WITH PERACETIC ACID

The following fibres were treated with 1·6% aqueous peracetic acid at laboratory temperature, with intermittent stirring— cow tail hair, rat hair, Devon hog wool. The cow tail hair was treated for 3 days, the rat hair for 2 days, and the Devon hog wool for 24 hr. The fibres, after treatment, were washed in several changes of distilled water, and allowed to dry. They were then embedded directly in ester wax without any dehydration, and sectioned. The outline of the cortical cells was visible on microscopic examination of sections of peracetic acid-oxidised fibres.

EMBEDDING AND SECTIONING

The embedding material used was ester wax, and the embedding was carried out in gelatin capsules (size 00) as used by Newman *et al.*[15]. Fibres were aligned and tied into bundles, which were then immersed in molten ester wax. The bundles were then placed in the capsules, which were filled with molten ester wax, and placed in water. As the wax solidified, precautions were taken to exclude air bubbles. On removal from the water, the gelatin had softened sufficiently to be easily removed from the wax block. The main advantage of using the capsules was that the fibre bundle was easily aligned. It was usually found that the cutting qualities of the block improved after a few days.

Transverse sections of 0·4–4·0μ. thickness were cut on a Cambridge rocking microtome, and the ribbons placed on water containing a little Cellosolve on a microscope slide. No adhesive was used. The slides were dried at 35–40°C., causing the sections to flatten. The wax was then removed by immersion of the slide in hot xylene, followed by a quick rinse in cold xylene.

It was observed that peracetic acid-treated fibres were more easily cut than untreated fibres.

PREPARATION OF SPECIMENS FOR MICROSCOPIC EXAMINATION

(*a*) TREATMENT OF PERACETIC ACID-OXIDISED SECTIONS WITH 0·1 N. AMMONIUM HYDROXIDE SOLUTION

Sections of peracetic acid-treated fibres on a microscope slide were covered with a cover-slip, and immersed in 0·1 N. ammonium hydroxide solution. Immediate swelling of the sections occurred. After 24 hr. the slide was removed

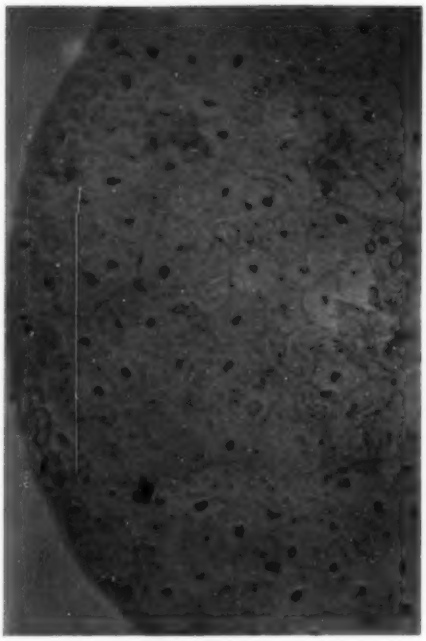


FIG. 1— Photomicrograph of Transverse Section of Peracetic acid-treated Cow Tail Hair, after Extraction with 0·1N. Ammonium Hydroxide; stained with Methylene Blue (425 ×)

FIG. 3— Electron Micrograph of Transverse Section of Peracetic acid-treated Devon Hog Wool, after Extraction with 2N. Sodium Hydroxide Solution (3,500 ×)

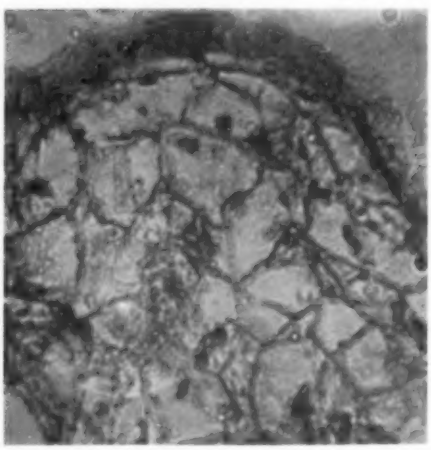


FIG. 2— Photomicrograph of Transverse Section of Peracetic acid-treated Devon Hog Wool, after Extraction with 2 N. Sodium Hydroxide Solution; stained with Methylene Blue (1000 ×)

FIG. 4— Electron Micrograph of Transverse Section of Devon Hog Wool, showing Part of a Membrane; Gold-shadowed, Negative Print (15,000 ×)

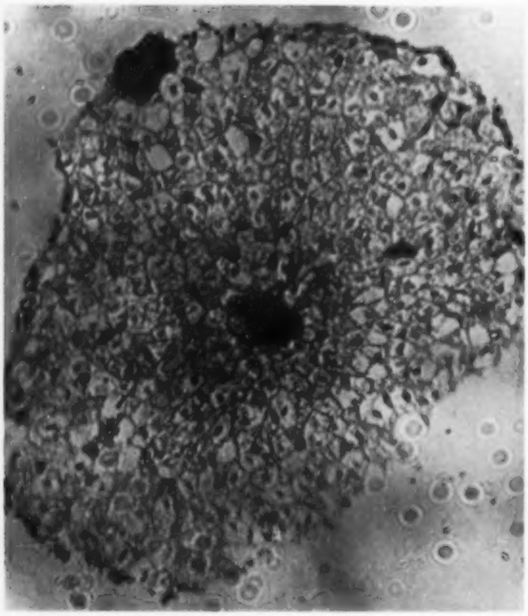


FIG. 5— Photomicrograph of Transverse Section of Unoxidised Cow Tail Hair after Treatment with 2 N. Sodium Hydroxide Solution; stained with Methylene Blue (310 ×)

FIG. 6— Electron Micrograph of Transverse Section of Cow Tail Hair after Sodium Hydroxide Treatment (2,000 ×)

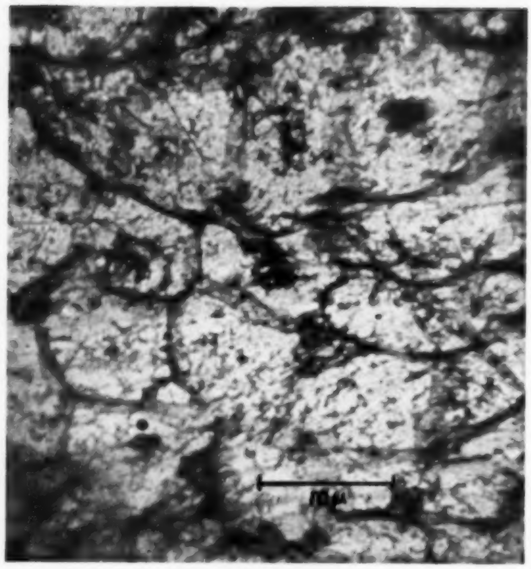


FIG. 7— Electron Micrograph of Transverse Section of Peracetic acid-oxidised Cow Tail Hair after 17 days in Pepsin (2,500 ×)

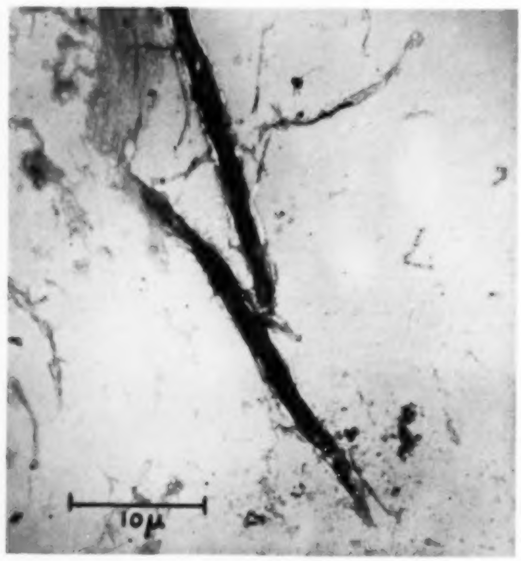


FIG. 8— Electron Micrograph of Remnants of Cortical Cell Nuclei, with some Fragments of Membrane, after Treatment of Merino Wool with Chlorine followed by Ammonium Hydroxide Solution (2,000 ×)

from the solution, and the sections were carefully washed with distilled water, and stained with methylene blue for optical microscope examination.

For electron microscope examination the sections after ammonium hydroxide treatment and washing were allowed to dry; the cover-slip was removed, and the slide then flooded with a 0·2% solution of cellulose nitrate in amyl acetate. The cellulose nitrate film with the sections attached could then be floated off on water, or stripped and examined. It was generally rather difficult to remove the film from the microscope slide, and stripping in 0·1N. ammonium hydroxide was more satisfactory.

It was found more convenient to extract the oxidised sections with sodium hydroxide solution instead of ammonium hydroxide, as this treatment was quicker and the extracted sections were more easily stripped from the slide. Optical microscope examination of sections of oxidised fibres extracted with either sodium hydroxide or ammonium hydroxide solution showed that they were similar in appearance. The oxidised sections were treated on a microscope slide with sodium hydroxide solution for 5–10 min., washed carefully with distilled water, and dried. The slide was flooded with a solution of cellulose nitrate, and the film floated off, or stripped from, the slide in water. The specimen grid was placed on the film under an optical microscope, and the filmed grids were picked up on filter paper, dried, and examined in the electron microscope. Some specimens were then shadowed with a heavy metal to increase the contrast [16].

Results

Optical microscope examination of transverse and longitudinal fibre sections, after these treatments, showed that parts of the cuticle, cortex, and medulla (where present) were resistant. Most of the material of each cortical cell had been dissolved, leaving the cortical cell boundary and remnants of the cell nucleus. Fig. 1 is an optical micrograph of a transverse section of a peracetic acid-oxidised cow tail hair after extraction with 0·1N. ammonium hydroxide solution and staining with methylene blue. Fig. 2 is an optical micrograph of a transverse section of a peracetic acid-oxidised Devon hog wool fibre, extracted with 2N. sodium hydroxide solution.

Electron-microscope examination showed that the resistant boundaries of the cortical cells were very thin membranes. Fig. 3 is an electron micrograph of a similarly treated transverse section of Devon hog wool. The membranes have fallen on their sides, they are creased longitudinally, and some fibrils adhere to them. The remnants of cell nuclei can sometimes be seen as opaque objects near the centre of the cells. Examination of gold-shadowed specimens shows that the membranes are of the same order of thickness as the epicuticle membrane, i.e. ca. 100 A.[17]. The electron micrograph in Fig. 4 is enlarged 15,000 times; the specimen had been shadowed at an angle of 4 to 1. Measurement of the shadow length on the photograph permits calculation of the thickness of the membrane forming the shadow, which is found to be of the order of 80–100 A. At the point at which the membranes of three adjacent cells meet, the membranes appear to be fused together.

Membranes have also been observed in the fragmented residues from whole merino wool fibres after peracetic acid and ammonium hydroxide treatment.

(*b*) TREATMENT OF SECTIONS WITH 2N. SODIUM HYDROXIDE SOLUTION

Sections of the following fibres were treated with 2N. sodium hydroxide solution—Lincoln wool, cow tail hair, and human hair. The untreated fibres were embedded in ester wax, and sectioned as described previously. Sodium hydroxide solution (2N.) was placed on the fibre section under a cover-slip, and the slide warmed at 60°C. for 7 min. After careful washing with distilled water until free from sodium hydroxide solution, the sections were stained with methylene blue for examination in the optical microscope.

For examination in the electron microscope, the sodium hydroxide solution was carefully washed from the slide, the slide dried, the cover-slip removed, and the sections were stripped on a cellulose nitrate film as described earlier.

Results

Optical microscope examination showed that the sections treated with 2N. sodium hydroxide solution were similar in appearance to those treated with peracetic acid and ammonium hydroxide. Fig. 5 is an optical micrograph, and Fig. 6 an electron micrograph, of transverse sections of treated cow tail hair. The thin membranes comprising the cortical cell boundaries are again clearly visible.

TREATMENT OF SECTIONS WITH SODIUM SULPHIDE SOLUTION

Gralén and co-workers [18] found that thin resistant membranes were obtained from wool fibres by prolonged treatment with 1% sodium sulphide. In the electron microscope these membranes were similar in appearance to the fragments of membranes separated by mild chlorination of wool [19]. This latter method of separation showed that the membrane came from the outermost layer of the cuticle, and it was termed "epicuticle". It has generally been assumed that the thin membranes separated by the sodium sulphide treatment of wool fibres were fragments of epicuticle. Since the membranes from the cortex of fibres are similar in appearance to the epicuticle membrane, it was decided to study the effect of sodium sulphide solution on fibre sections.

Transverse sections of untreated cow tail hair were treated under a cover-slip with 1% sodium sulphide solution at 60°C. for 3½ hr. After this treatment, cortical cell outline was visible under the optical microscope. The sodium sulphide solution was carefully washed away with distilled water, the slide dried, the cover-slip removed,

and specimens were prepared for electron microscope examination as before. The cortical cell boundary membranes were again seen, showing that these membranes were resistant to the treatment.

TREATMENT WITH PROTEOLYTIC ENZYMES

Peracetic acid-oxidised fibres were placed in 0·2% pepsin solution at pH 1·2 and 40°c. for several days. No cortical cells were liberated, but most of the cortex was digested. Transverse sections of oxidised fibres, supported on a cellulose nitrate film, were floated on pepsin solution. After a few days' treatment, the cortical cell outline was visible under the optical microscope. Fig. 7 is an electron micrograph of a peracetic acid-treated cow tail hair section, after seventeen days' digestion. Most of the material of the cortical cells had been removed, but the membranes were resistant to this period of treatment. Thus, in the peracetic acid-treated wool the membranes were more resistant than the rest of the fibre.

Pepsin digestion separates cortical cells from untreated wool, and from reduced-and-alkylated wool [20]. Fibres were reduced and alkylated by the method of Brown, Pendergrass, and Harris [21], and the fibres treated with 0·5% pepsin solution. Attempts were made to identify membranes from cortical cells which had been separated. The fibre residues after digestion were ground with a little water, and the suspension was examined in the electron microscope. No membranes were visible.

Peracetic acid-treated merino wool fibres were treated also with 0·5% trypsin solution at pH 8 and 40°c. After 20 min. treatment the whole of the cortex dissolved, leaving sheets of epicuticle which readily fragmented. Sections of peracetic acid-treated cow tail hair placed in trypsin solution at pH 8 were observed under the microscope. Immediate and rapid swelling occurred, and the cortical cell outline was visible for a short time. Finally, the whole of the section appeared to dissolve. From these experiments, it can be concluded that the membranes from the cortex are dissolved by proteolytic enzymes.

TREATMENT OF FIBRES WITH CHLORINE AND AMMONIUM HYDROXIDE SOLUTION

Fibres were oxidised with acidified hypochlorite solution (50% chlorine on the weight of the fibre) and extracted with ammonium hydroxide solution. Although considerable swelling of fibres and fibre sections occurred, cortical cell outline was not visible. No membranes were visible when treated sections were examined in the electron microscope. However, the residues from whole fibres were found to contain some fragments of membranes, with remnants of the cortical cell nuclei (Fig. 8). The remnants of the nuclei, which are 30μ. long and 1·5μ. wide, appear fibrous.

Discussion

One of the earliest references to a layer which lies directly below the cuticle of wool fibres was made by McMurtrie [2], who suggested that the cuticle cells of wool were held together by an underlying submicroscopic membrane. This suggestion was made to account for the sheaths of cuticle material which are obtained when wool fibres are given a short-time treatment with sodium hydroxide solution. Sheaths of material similar in appearance under the optical microscope are obtained in the residue from wool after treatment with peracetic acid, followed by extraction with 0·1N. ammonium hydroxide solution. It seems probable that the sheath obtained in each case derives from the resistant epicuticle.

It has been claimed that any of the following treatments isolate the "subcuticle membrane"—

(*a*) Treatment of wool with formaldehyde solution at 140°c.[22]

(*b*) Tryptic digestion of wool which has been supercontracted in phenol [23]

(*c*) Treatment of wool with 1·6% aqueous peracetic acid, followed by extraction with 0·1N. ammonium hydroxide solution [9]

(*d*) Treatment of fibres with sodium hydroxide solution [8,11]

(*e*) Treatment of fibres with pancreatin, followed by concentrated sulphuric acid [11].

Treatments (*a*) and (*b*) were later investigated by Mercer, Lindberg, and Philip [14], who examined the resistant components present, and found them to contain epicuticle. However, Alexander, Zahn, and Haselmann [7] have pointed out that the chemical methods of separation of the "subcuticle membrane" yield also varying amounts of cuticle. The "subcuticle membrane" was identified under the optical microscope, and was said to be 0·3μ. thick for the wool fibre [8]. If the residues were in fact a layer between the cuticle and the cortex of the fibre, a transverse section after treatment with sodium hydroxide solution, or peracetic acid followed by ammonium hydroxide solution, would have appeared as a ring of resistant material left from the outside of the cortex.

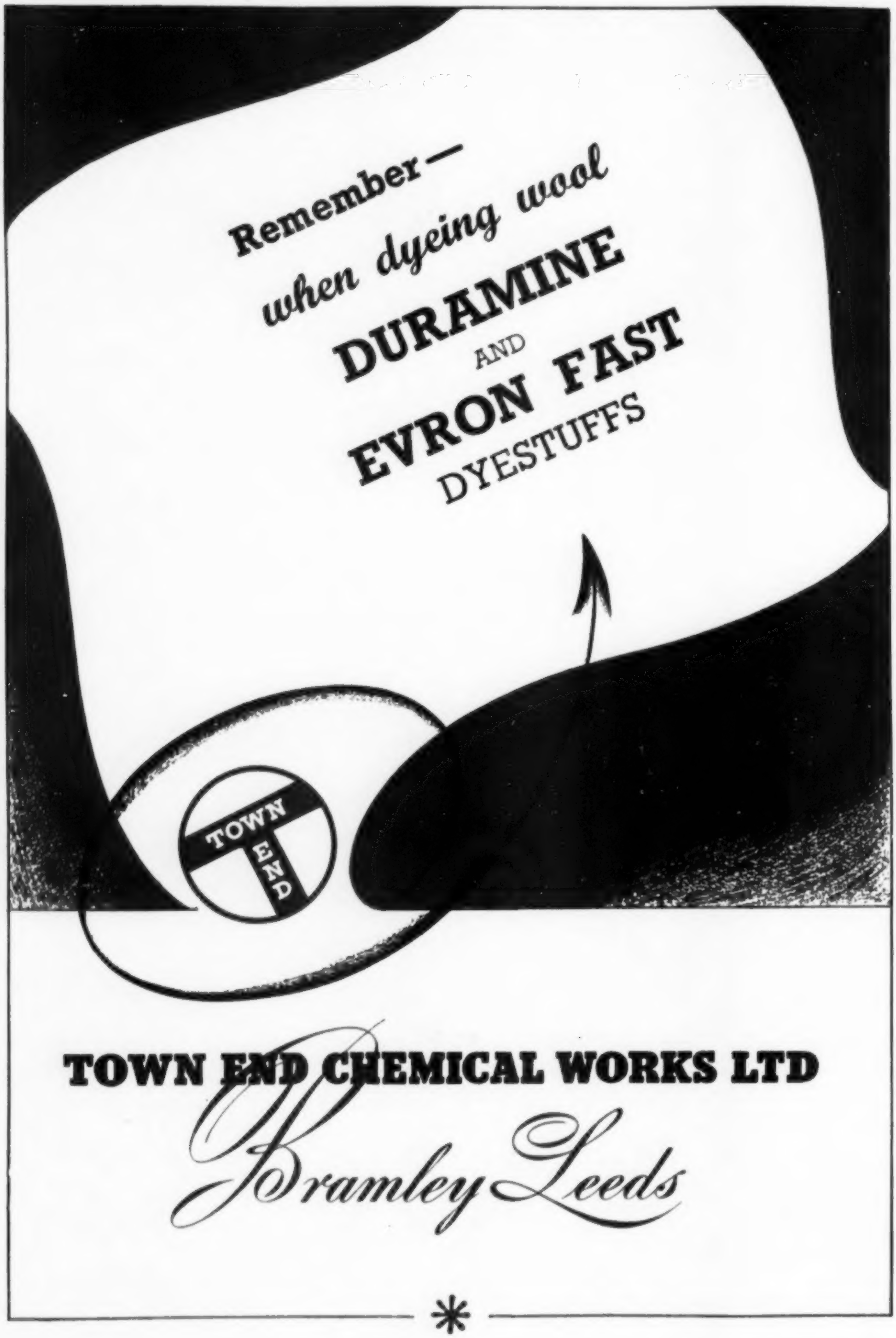
It can be seen from the preceding micrographs of treated sections that the residues consist of parts of the cuticle, cortex, and medulla. The cortex component comprises cortical cell boundaries (which are thin membranes), remnants of cortical cell nuclei, and fibrils. The experiments thus show that the "subcuticle membrane" is not isolated by these treatments. Similar conclusions were reached by Mercer [25,26], who examined sections of wool and hair fibres in the optical microscope after treatment with peracetic acid and ammonium hydroxide.

In the fully keratinised cortex there are thus two phases— a continuous (membrane) phase and a discontinuous (cellular) phase.

It is not possible to decide from electron micrographs whether the membranes from the cortex are single or double, i.e. whether they should be termed cell walls or cytoplasmic cell membranes. If they are cell membranes, it is possible that, during the growth of the fibre, membranes of adjacent cells fuse together.

Although the epicuticle and the membranes from the cortex show many similarities, they must


Secret + confidential
Two highly efficient agents for penetrating and wetting
Nervan CFB
An alkyl aryl sulphonate of outstanding stability to acids, alkalis and divalent salts
Anonaid T—a sodium dioctyl sulpho-succinate. It's no secret that it is unequalled in efficiency even at the lowest concentration
NORMAN EVANS & RAIS LTD.
Dudley Road · Manchester 16 Tel: MOSs Side 2277
Anonaid T
NER 5


Remember—
when dyeing wool
DURAMINE
AND
EVRON FAST
DYESTUFFS
TOWN
END
TOWN END CHEMICAL WORKS LTD
Bramley Leeds

differ, since the membranes from the cortex are dissolved by trypsin, whilst the epicuticle is not.

The chemical composition of membranes separated from wool fibres by mild halogenation, or prolonged action of sodium sulphide, has been investigated [27–30] and found to be mainly protein. Schuringa has found [28] that 0·7% by weight of wool is resistant to the action of sodium sulphide, although the epicuticle would account for only 0·2% at most. It would thus appear that determinations which have been performed on the chemical composition of the residues resistant to sodium sulphide solution give the composition of a mixture of epicuticle membrane and the membranes from the cortex.

The proportion of a fibre resistant to peracetic acid and ammonium hydroxide solution, or to sodium hydroxide solution, has been given as 4–10% by weight of the fibre. Of the treated sections, a much smaller percentage by weight is apparently resistant, probably because material is more readily removed from sections than from whole fibres.

Remnants of cortical cell nuclei are visible in treated sections, whilst whole fibre residues contain additional fibrous material.

Of the chemical treatments used in this investigation, enzymic digestion of reduced-and-alkylated fibres, or of untreated fibres, were the only ones which separated cortical cells, and in these preparations we were unable to identify membranes. The other treatments used did not isolate the cortical cells, but membranes were observed in treated sections. It seems, therefore, that the membranes of the cortex of untreated or reduced-and-alkylated fibres are more susceptible to enzyme digestion than the rest of the fibre. The membranes from the cortex may therefore be the material hitherto termed "intercellular cement". It is interesting to record that Olofsson [31] suggested that the substance in wool sensitive to trypsin digestion is like a net of fine membranes, which enclose fibrous material, and a similar suggestion was made by Auber [32].

* * *

We wish to thank the Bradford Dyers' Association Ltd. for a fellowship (to B.M.) and the Wool Textile Research Council for a scholarship (to M.S.M.).

CHEMISTRY AND DYEING DEPARTMENT
TECHNICAL COLLEGE
BRADFORD

(*Received 10th March 1954*)

References

1. Nathusius, W., *Das Wollhaar des Schafes in histologisher und technischer Beziehung* (Berlin 1866).
2. McMurtrie, W., *Examination of Wools and Other Animal Fibres* (U.S. Government Printing Office. 1886).
3. Bowman, F. H., *Structure of the Wool Fibre* (London: Palmer & Howe. 1885).
4. Burgess, R., *J. Textile Inst.*, **25**, T 289 (1934).
5. Reumuth, H., *Melliand Textilber.*, **23**, 1, 53 (1942).
6. Wildman, A. B., and Manley, J., *Trans. Roy. Soc. Edin.*, **59**, (II), 333 (1937–38).
7. Alexander, P., Zahn, H., and Haselmann, H., *Text. Research J.*, **21**, 236 (1951).
8. Zahn, H., *Melliand Textilber.*, **31**, 36 (1950).
9. Alexander, P., and Earland, C., *Text. Research J.*, **20**, 298 (1950).
10. Alexander, P., *Nature*, **168**, 1081 (1951).
11. Zahn, H., and Haselmann, H., *Melliand Textilber.*, **31**, 225 (1950).
12. Manogue, B., and Elliott, R. L., J.S.D.C., **69**, 113 (1953).
13. Gralén, N., Philip, B., and Lagermalm, G., *Text. Research J.*, **21**, 234 (1951).
14. Manogue, B., and Moss, M. S., *Nature*, **172**, 806 (1953).
15. Newman, S. B., Borysko, E., and Swerdlow, M., *Bur. Stand. J. Res.*, **43**, 183 (1949).
16. Williams, R. C., and Wyckoff, R. W. G., *J. Applied Phys.*, **18**, 23 (1946).
17. Mercer, E. H., Lindberg, J., Philip, B., and Gralén, N., *Text. Research J.*, **19**, 673 (1949).
18. Lindberg, J., Philip, B., and Gralén, N., *Nature*, **162**, 458 (1948).
19. Lindberg, J., *Text. Research J.*, **19**, 678 (1949).
20. Hock, C. W., Ramsay, R. C., and Harris, M., *Bur. Stand. J. Res.*, **27**, 181 (1942).
21. Brown, A. E., Pendergrass, J. H., and Harris, M., *Text. Research J.*, **20**, 51 (1950).
22. Lehmann, E., *Kolloid-Z.*, **108**, 6 (1944).
23. Elöd, E., and Zahn, H., *Naturwiss.*, **33**, 158 (1946).
24. Mercer, E. H., Lindberg, J., and Philip, B., *Text. Research J.*, **19**, 678 (1949).
25. Mercer, E. H., *Nature*, **172**, 164 (1953).
26. Mercer, E. H., *Text. Research J.*, **23**, 388 (1953).
27. Lagermalm, G., and Gralén, N., *Acta Chem. Scand.*, **5**, 1209 (1951).
28. Schuringa, G. J., Isings, J., and Ultée, A. J., *Biochim. et Biophys. Acta*, **9**, 457 (1952).
29. Schuringa, G. J., Schooneveldt, C. J., and Ultée, A. J., *ibid.*, **9**, 506 (1952).
30. Ultée, A. J., Schooneveldt, C. J., and Schuringa, G. J., *ibid.*, **10**, 590 (1953).
31. Olofsson, B., *Medd. Svenska Textilforskningsinst. Göteborg*, (2), 2 (1946).
32. Auber, L., *Proc. Roy. Soc. Edin.*, **62**, 1, 191 (1950).

Notes

Meetings of Council and Committees October

Council— 20th

Finance— 20th

Publications— 19th

Colour Index Editorial Panel— 26th

Diplomas Executive Subcommittee— 6th and 27th

The Earliest Record of Indigo Dyeing in England

Mr. L. E. Morris has presented to the Society's Committee for the Preservation of Historical Records a transcript of one of the documents in the Lansdowne Manuscripts in the British Museum (*Lansdowne MSS.*, **24** (66)), which deals with what apparently was the first appearance of Indigo in England. There is nothing to show to whom the document was sent, but it seems to be a memorandum drawn up for, perhaps, the Privy Council.

This document is of such interest and importance that the transcript is reproduced in full below.

Recto

Whereas one Pero Vaz Devora portuguese is sente from the king of Portugale into this Realme to make shewe and triall of the working of a certein commodity or merchandize named Aneel commonly called in English Blue ynde which commeth out of the East yndias and by reporte is made of the flower and first croppe and cutte of an herbe growing there whereof woade is made not before this tyme practized uppon wull or clothe in Englande. The said Pero Vaz hath accordinglie shewed howe to use and occupie the same, to us the diars and merchannts hereunder named and others, severall tymes in the citie of London, being sett and putt to worke with certein quantitie of woade in the common woade fats used in London, which have wrought kindlie and dutlie [*] toguether, and have made perfit and durable colour of Blue, Azure and Watchets according to the nature of goode Woade. And the commoditie [convenience] that wee do finde by the same Aneel is that fortie shillings bestowed in the same, yeldeth as much colour as fiftie shillings in woade, or (for more plaine understanding) iiij li waighte of the same prised at fortie shillings, yeldeth as much colour to our iudgement as one hundreth weight of Tholose [Toulouse] woade nowe worth fiftie shillings, and maketh more oryent [brighter] colour, and we saie that uppon this triall the same commoditie will and maie hereafter be occupied in this citie uppon clothe, and wilbe profitable in divers respects, if it maie be had at reasonable price, but we esteem it to be too deer at X ss. the pounde, for that woade will fall of the price that now is, god sending more quiet tyme.

Also the said Pero Vaz saieth that he is readie to shewe the proof of the same Aneel upon wulls unwroughte, if he be sent to places in the cuntrie where it is most used [i.e. where dyeing of "wulls unwroughte" is most practised], and affirmeth that it is more profitable and goeth further and it will be better liked to die wulls unwroughte, which is most commonlie used throughout all Englande.

* Presumably *doughtily*, i.e. strongly or powerfully, but it may be "ducely", i.e. doucely, quietly or steadily. The letters *t* and *c* sometimes look much alike in old forms of handwriting. [L.E.M.]

In witness whereof we have herunto subscribed our names, dated in London the XXVII[th] daie of Aprile 1577 anno RR Eliz. XIX°

By me Robert Dow [?]	By me John Bayly dyer
By me Rychard May	By me Rychard Cooper dyer
By me Donston Ames [?]	By me William Glover dyer

Verso

May 1577

The testimony of y[e] merchannts and dyars tuching the practise of Pero Vas Devora in dyeing with Aneel.

In Suffolk	Lavenham [†] Hadley
In Berksh.	Redyg Nubury
In Hampshir	Fareham

It would seem that the information contained in this document was acted upon, for in 1581 the Act of 23 Eliz. permitted English dyers to use "Anele alias Blue Inde" along with woad for bottoming blacks on wool, but under James I the woad interests prevailed upon the Government to pass an Act prohibiting the use of Indigo. This Act remained in force until the reign of Charles II, when Flemish dyers had to be brought to England to reintroduce the technique of Indigo dyeing.

C O C

† This list of places is scrawled faintly below the title of the memorandum and appears to have been added afterwards. Perhaps it is a note of the "places in the cuntrie" where Pero Vaz Devora was prepared to demonstrate the use of Indigo on "wulls unwroughte". [L. E. M.]

Seventh O.C.C.A. Technical Exhibition
London, 15-17th March 1955

The Exhibition will take place at the Royal Horticultural Society's Old Hall, Vincent Square, S.W.1, the times of opening being 3–8.30 p.m. (March 15th) and 11 a.m.–7 p.m. (March 16th and 17th). The theme of the exhibition will be the presentation of technical advances in those industries supplying the paint, varnish, printing ink, linoleum, and allied industries. The technical advances may relate to new products, new knowledge relating to existing products and their uses, or, in suitable cases, existing knowledge which is not generally available in the consuming industries. Full details may be obtained from the Oil and Colour Chemists' Association, Memorial Hall, Farringdon Street, London E.C.4 (CENtral 2120).

Sixth Canadian High Polymer Forum
St. Catherines, Ontario, 14-15th April 1955

This forum, which is devoted to all aspects of high polymer chemistry, will be held at Ridley College. Contributions to the forum should be sent as soon as possible to the programme chairman, Dr. H. L. Williams, Research and Development Division, Polymer Corporation Ltd., Sarnia, Ontario, and confirmed with a two-hundred-word abstract not later than February 15th. Enquiries regarding accommodation should be directed to Mr. D. S. Fensom, of Ridley College. General information on the forum can be obtained from the Secretary-Treasurer, Dr. D. G. Ivey, Department of Physics, University, Toronto, Ontario.

Second International Textile Exhibition

Brussels, 25th June to 10th July 1955

This exhibition, which will be housed in the Palais du Centenaire, Brussels, will include dyeing and finishing requisites, chemical products, trade and specialised publications, and research and information. Full details may be obtained from the General Secretariat, Second International Textile Exhibition A.S.B.L., 15 rue des Drapiers, Brussels, Belgium.

New Books and Publications

The Physical Chemistry of Dyeing and Tanning

Discussions of the Faraday Society No. 16

The Faraday Society. Pp. 251 (+5). Aberdeen: Aberdeen University Press Ltd. 1954. Price, 35s. 0d.

This General Discussion, held in the Department of Chemistry of Leeds University during 8–10th September 1953, continued the tradition of the Faraday Society in bringing together workers, both British and foreign, in a given field of physical chemistry. The General Introduction, by Sir Eric Rideal, sets out clearly the present state of dyeing theory, and the problems to be solved before it can be freed from empirical factors.

The scope of this General Discussion is shown more clearly by the list of papers given below. Abstracts of all the papers relating specifically to dyeing will be found in this issue of the *Journal*.

The Kinetics of Acid Absorption on Wool Fibres R. F. Hudson

The Combination of Acids and Colour Acids with Keratin L. Peters and G. H. Lister

A Contribution to the Theory of Diffusion of Sorbed Substances into and out of Fibres B. Olofsson

Study of Diffusion Processes in Tanning D. M. G. Armstrong

The Self-diffusion of a Dye in a Polar Polymer Membrane M. L. Wright

The Absorption of Sodium Sulphate and Sulphuric Acid by Hair D. L. Underwood and H. J. White, Jr.

The Kinetics of Absorption of Water and Aqueous Solutes by Dry Viscose Cellulose H. B. Mann and T. H. Morton

Theoretical Aspects of the Dyeing of Cellulose Acetate Rayon C. L. Bird, F. Manchester, and Miss P. Harris

Researches on Monolayers. IV — A Study of Dyeing Processes by the use of the Unimolecular Film Balance Miss Margaret M. Allingham, C. H. Giles, and E. L. Neustädter

Atomic Models. III — Some Stereochemical Problems in Dyeing Conmar Robinson

The Adsorption of Dyes by Crystals J. Whetstone

Calorimetric Studies of the Reaction of Naphthalene Orange G with Amino Acids A. N. Derbyshire and W. J. Marshall

The Solubility and Activity of Orange II in Sodium Chloride and Sodium Sulphate Solutions A. B. Meggy

The Selective Absorption of Optical Antipodes by Wool W. Bradley, R. A. Brindley, and G. C. Easty

Tanning of Fatty Acid, Amino Acid, and Protein Monolayers by Metal Ions J. H. Schulman and M. Z. Dogan

The Interaction of Tanning Materials with Collagen Monolayers S. C. Ellis and K. G. A. Pankhurst

Viscosimetric Study of the Hardening of Gelatin by Chrome Alum J. Pouradier

Some Aspects of the Reaction of Basic Chromium Salts with Hide Protein K. H. Gustavson

Mucoid Material in Hides and Skins and its Significance in Tanning and Dyeing D. Burton and R. Reed

Mechanism of Absorption of Non-ionic Dyes by Polyethylene Terephthalate M. J. Schuler and W. R. Remington

The Dyeing of Polyacrylonitrile Fibres with Anionic Dyes R. H. Blaker, S. M. Katz, J. F. Laucius, W. R. Remington, and H. E. Schroeder

The Dyeing of Synthetic Polypeptides C. H. Bamford, J. Boulton, W. E. Hanby, and J. S. Ward

C. J. W. H.

Anilinfesték-Könyv

(Hungarian Dyestuff Book)

II

A Magyar Ipar Használatára

Edited by Gáspár Soltész and Aladár Bokor. Pp. 232 (First Part) + 300 (Second Part). Budapest: Az Országos Tervhivatal Kiadványa. Forgalomba Hozza: Nyomtatványellátó Nemzeti Vállalat. 1950. Price, 65s. 0d.

Although the preface of this volume states: "The first volume of this work published six months ago has treated of the dye-stuffs employed in the textile industry", the English agents state (1954) that Volume I has not been published. It is therefore difficult to assess the precise scope and the objectives of the whole work, and it is only possible to assume certain facts by the method of treatment and general directives given in Volume II.

The general text is quadrilingual— Hungarian, Russian, English, and German— but the bulk of the pages are devoted to lists of commercial names of dyes in the language of their origin.

The following non-textile usage groups are covered in Volume II—

PART 1

Wood, metal, glass, and porcelain
Plastics
Paper
Inks, crayons, fine chemicals
Leather

PART 2

Fur
Rubber
Vegetable oil, fat, and soap
Lakes, printing inks, mineral oils, and domestic chemicals
Cosmetics
Foodstuffs
Medicinal, pharmaceutical

Each of these sections contains lists of commercial names of dyes with the manufacturers' initials, equivalent products being grouped together and each group carrying a five-digit reference number which is based on a 00.000 decimal system. At the end of each section there is an alphabetical index of the dyes listed.

There is very little information on chemical constitution apart from the inclusion of *Colour Index* or *Schultz* numbers in some cases. This is not consistent, as shown by the absence of *C.I.* numbers against the well known dyes "Direct Black E" and "Direct Black BH", which are *C.I.* 581 and *C.I.* 401 respectively. Exceptions are

the oxidation bases for application to fur and the dyes listed for cosmetics and foodstuffs, for which data on constitution are given.

This publication will be useful mainly as a means of indicating broadly those industries using certain types of dyes in Hungary, and in addition it is useful as a fairly up-to-date set of lists of equivalent or identical products of different commercial names. No attempt has been made by the reviewer to test the accuracy of these groups of equivalents. Products of all the main European and American dye manufacturers are listed. It contains the products marketed by some dye manufacturers in Europe information on which is not readily available from other sources.

The arrangement of dyes into industrial uses results in fairly considerable repetition of lists. A weakness of the book lies in grouping together in some sections a wide variety of only loosely connected uses— e.g. wood, metal, glass and porcelain — without indicating the specific uses of the individual dyes.

This publication, which could be regarded as a type of *Colour Index*, appears to be a useful addition to the list of such works of reference. The quality of the production is moderate but adequate. It is bound on the spiral-spring principle.

H. BLACKSHAW

Vegetable Tanning Materials

By F. N. Howes. Pp. xi + 325. London: Butterworths Scientific Publications. 1953. Price, 35s. 0d.

This book gives, in a very readable form, a considerable amount of information about all the principal vegetable tanning materials and a great many of the lesser known ones.

In a 23-pp. introduction the author gives a brief but sufficient outline of the chemical nature and classification of the natural tannins and deals in some detail with the factors influencing the distribution and function of the tannins both throughout the vegetable kingdom and within the individual plants. The introduction includes also a historical review of the uses of tannins and covers the present-day applications, concluding with some notes on the manufacture of tannin extracts and the world trade in vegetable tannins. One minor criticism is the author's implication on p. 15 that the vegetable tannins are the only means of tanning leather. The significance and necessity for this statement are far from obvious, and it is liable to be misleading.

The main portion of the book deals with the important tannin materials individually and classifies them under Barks, Woods, Fruits, Leaves, Roots, or Galls according to the part of the plant in which the tannin is found. Where a tannin material occurs in different parts of the same plant, the tannins from each part are dealt with as separate products, under the appropriate sections. Thus, oak is to be found under woods, barks, and also galls. The space devoted to each tannin material is roughly proportional to its importance. Based upon the author's first-hand knowledge of South Africa, the section on the black wattle is particularly full and interesting and covers all aspects from the cultivation of the tree to the use in tanning of the finished tannin extract.

In a chapter on Miscellaneous Tanning Materials are collected brief notes on over 300 plants which either have been used at some time as a source of tannin or alternatively have been shown to contain at least 10% tannin, calculated on the dry weight. This figure is taken as an indication that the material contains sufficient tannin to make it a potential source, other factors being favourable.

Throughout the book, tan contents are quoted, but unfortunately the corresponding non-tan figures are not often included.

The use of the common names, in addition to the botanical names, makes the book suitable for the general as well as the scientific reader. A list of over 800 plants under their botanical names is supplemented by a good general index, and a comprehensive list of references is also included.

Much thought has obviously gone into making the book a handy source of information, for, apart from the above-mentioned indexes, the chapters are divided into short sections with subheadings which are reproduced at the tops of the relevant pages.

The printing of the book and the reproduction of a number of plates and diagrams leave nothing to be desired.

J. K. HUSSELBY

BS 2490 : 1954
Waterproof Drawing Inks

Pp. 14. London: British Standards Institution. Price, 3s. 0d.

This standard gives eleven colours (designated BS(D1) colours) together with their C.I.E. values and their Lovibond–Schofield Tintometer readings. Standards of fastness to light and solvents and draughting, erasing, and keeping properties are included. Appendixes describe the preparation of test samples and the methods of testing the waterproof and free-flowing properties of inks.

C. O. CLARK

The Design and Analysis of Industrial Experiments

Edited by Owen L. Davies. Pp. xiv + 637. London and Edinburgh: published for Imperial Chemical Industries Ltd. by Oliver & Boyd. 1954. Price, 63s. 0d.

This book is a sequel to *Statistical Methods in Research and Production, with special reference to the Chemical Industry*, edited by O. L. Davies and published in 1947 (reviewed in J.S.D.C., **64**, 154 (1948)). The earlier volume has had a considerable success, many students of statistics finding in it a simple, concise introduction to the subject, with a balanced blend of theory and application, the subject being taken to the fringe of experimental design and analysis of variance techniques. The present volume will therefore be welcomed by those who have to try to interpret experimental results depending on a complex physical structure, and who are familiar with the basic ideas of statistical method, including simple tests of significance such as Student's t and the F ratio test.

Until recently, most of the books on experimental design have had a decided agricultural or biological bias. Moreover, although there is a fundamental basis to all experimental design, applications in different fields may demand special and unique developments. Dr. Davies and his collaborators have produced a volume which shows the special application of statistical design in industrial chemistry.

There are eleven chapters in the book, the second chapter dealing with simple comparative experiments, explaining the meaning of randomisation and confidence limits, and giving tests for the comparison of means and variances. In this chapter there is also introduced the idea of the Operating Characteristic Curve for a test, methods of variance stabilisation, and transformations towards normality.

Chapter 3 makes a special feature of the application of sequential tests of significance. In many experiments the choice of the number of observations to be made to reach a conclusion has to be made in advance. But sequential tests (developed by Wald in America and Barnard in this country during the 1939–1945 War) are designed to reach a decision as soon as the experimental evidence warrants it, due regard being paid to the risks involved.

Chapter 4 deals with the investigation of sampling and testing methods, and introduces the idea of main and differential effects in an experiment. The simplest balanced designs are discussed, and the foundation is laid for more complicated designs, having touched on such basic notions as error and its assessment, bias, reproducibility, and components of variance. There are several examples worked out in detail, and a brief theoretical background is given in six appendixes to the chapter.

Randomised blocks, useful when several experimental treatments under almost constant conditions are to be compared, Latin squares (a variation of the randomised block), which are useful when effects are independent, Graeco-Latin squares, and Latin cubes are discussed in Chapter 5.

There are three chapters on factorial experiments, which deal with the analysis of experiments involving two or more factors each at several levels. Since the size of a factorial experiment increases rapidly with the number of factors, various devices are required aimed at extracting relevant information and ignoring the unimportant or foreseeable. One such device, that of confounding, is described in Chapter 9.

Chapter 10, on fractional factorial experiments, cites as examples the filtration conditions during the preparation of a dye and the quality of a basic dye.

Chapter 11 describes the design of experiments so that the best operating conditions involving several factors can be found. Theoretically, this is equivalent to finding the maxima (or minima) of a function (the response function) of several variables, the form of the function being approximated by the first few terms of a polynomial expansion. The ideas are clearly illustrated by considering a response function depending on two factors, showing how the peaks, troughs, ridges, etc. appear in the response contour diagrams. There can be little doubt that the general approach outlined in this chapter of some eighty pages should have many applications in subjects allied to chemistry.

The authors' preface indicates that the book is written principally for the research worker in the chemical industry with a limited knowledge of mathematics. It certainly will be of great value to any student of statistics (irrespective of the applied field) who proposes to acquaint himself with the basic ideas underlying experimental design, and to any worker in the technological sciences who has to test hypotheses through experiment. There is a considerable store of statistical experimental data and its interpretation in this volume, all arising from actual practice, and this alone should make it an indispensable book for anyone learning more about the subject.

L. R. Shenton

Work Study Conference Proceedings
Buxton, 9–10th October 1953

Pp. v + 147. London: Association of British Chemical Manufacturers. [1954.] Price, 12s. 6d. (7s. 6d. to A.B.C.M. members).

This conference was organised by the A.B.C.M. in order to implement one of the recommendations of the Heavy Chemicals Productivity Team which had visited the U.S.A. in the spring of 1952.

A number of papers on the different aspects of Work Study were given by members of the staff of Imperial Chemical Industries Ltd., and were followed by discussions of some of the implications of the introduction of Work Study. The published proceedings give a full report of the formal papers and the discussions.

Work Study, in brief, consists in the critical examination of present methods of working and of organisation with the object of improving operational efficiency. There are in general six lines of attack to increase productive efficiency —

1. Improve basic processes by research and development.
2. Improve existing and provide better plant and equipment.
3. Standardise and simplify the product and reduce the variety.
4. Improve the methods of operation of existing plant.
5. Improve the planning of work and the utilisation of manpower.
6. Increase the effectiveness of all employees.

Work Study is conveniently divided into the two interdependent techniques of Method Study and Work Measurement.

Method Study has three essential aims —

1. To reveal and analyse fully the true facts concerning any situation.
2. To examine these facts critically.
3. To develop from the examination of the facts the best answer possible in the circumstances.

Work Measurement consists in arriving at the work content of a job by actual observation, by synthesis from standard data or from analytical estimating, and the results can form the basis of a financial incentives scheme. Details are given of the bases of a number of different types of such schemes.

The proceedings of the Conference are a valuable addition to the literature on Work Study, and should prove of interest to managements considering the introduction of Work Study or concerned with the increasing of operational efficiency.

Abstracts from British and Foreign Journals and Patents

The titles of abstracts may be modified. Abbreviations of names of firms are listed in J.S.D.C., **68**, *23 (Jan. 1952), and also, together with symbols and the periodicals abstracted, in the annual index*

I—PLANT; MACHINERY; BUILDINGS

PATENTS

Supports for Yarn Cakes during Wet Processing. E. A. Stienen. *BP* 714,945

An improved and economical method for uniformly compressing the cake to a predetermined density so that even dyeing is readily attained. C. O. C.

Apparatus for applying Liquids to Yarns. ICI. *BP* 713,276

Liquids are applied to moving yarn by a roll or wheel which collects a film of liquid on its peripheral surface and thus conveys it to the yarn. The wheel surface must be of a very hard abrasive, e.g. carborundum, which is cheaper than the conventional glass, has a much longer life, and appears not to damage the filaments. J. W. B.

Package Dyeing and Drying of Yarn. Mellor Bromley & Co. *BP* 714,435

A simple efficient fastening device which prevents the packages moving relative to the spindles and which automatically adjusts itself to compensate for shrinkage of the yarn. C. O. C.

Safety Guard for Milling Machine. Richard Kilburn & Sons. *BP* 714,920

The guard moves about its axis and has a pendant link pivotally attached to it. This link is associated with the draft board by a lost motion or similar action so that raising the guard automatically lifts the draft board and stops the machine. The board can lift relative to the guard without disturbing the latter but the board cannot be pulled down without moving the guard into its working position. C. O. C.

Open-width Washer. D. Dukerts. *BP* 713,936

The cloth is treated in a series of separate vessels or compartments in the first of which it is acted upon by a beating element, e.g. a roller covered with projections, actuated by an alternating and partly rotary motion. In each of the other compartments the cloth passes over or under a roller through which the washing liquor is circulated so as to form a closed liquor circulation system in each compartment. The arrangement is such that in each washing compartment the liquor is sucked through the cloth and then sprinkled on to it. C. O. C.

Electric Control System for Maintaining Registration of a Moving Web. Westinghouse Electric International Co. *BP* 714,971

A system of control which is equally responsive to transverse shifting of the selvedge or of a line or mark running longitudinally to the material being processed. C. O. C.

Selvedge Guides. R. Meissner. *BP* 713,874

Back Grey. J. Verduin. *BP* 715,021

An improved form of back grey is made of a partly absorbent material, e.g. nylon or Orlon, and is run as an integral surfacing of an endless deformable blanket passing between the printing cylinder and the fabric being treated. It also passes through a washer and a drier so that it is always in cleansed, renewed condition at the printing position.

BP 715,107

The blanket consists of a fluid-impervious base material to which the absorbent textile layer is bonded. C. O. C.

All-metal Printing Screens. J. B. Brennan. *BP* 714,766

The resist on a wire screen is made by applying finely divided metal which is then sintered to bond the particles to each other and to the screen. Preferably the metal powder is applied to the wire screen through a silk screen, the powdered screen being then heated to sintering temperature while clamped between smooth rigid plates. C. O. C.

Dipping, Stretching, Compressing, Drying and Winding Rovings and Yarn (VI p. 518).
Electrodeposition and the Printing Trade (IX p. 522).
Cotton Finishing Developments (X p. 523).
Recovery of Solvents used in Long Webs (X p. 524).

III—CHEMICALS; AUXILIARY PRODUCTS; FINISHING MATERIALS

Manufacture of Chlorine Dioxide. H. Tydén. *Svensk Papperstidning*, **57**, 583–590 (31 Aug. 1954).

PATENTS

Washing and Milling Agents. "Tepha" Ges. für Pharmazeutisch und Chemisch-Technische Erzeugnisse. *BP* 715,017

A mixture of (*a*) a condensate of a water- or alkali-soluble protein or protein degradation product with a soap-forming acid and (*b*) an alkali metal salt of an alkylbenzenesulphonic acid is an excellent detergent and milling agent and may be used in an acid bath. C. O. C.

Water-soluble Phytates as Builders for Detergents. Proctor & Gamble Co. *BP* 714,212

The water-soluble salts of phytic acid are useful building agents for use with organic detergents. C. O. C.

Yarn Lubricant. Celanese Corpn. of America. *USP* 2,637,693

A yarn lubricating and conditioning composition consists of a mixture of a mineral oil, an aryl phosphate (e.g. triaryl phosphate), a long-chain aliphatic acid (e.g. oleic acid), an alkylolamine, a little of a blending agent (e.g. oleyl alcohol) or a multi-component conditioning agent. The latter is prepared by treating a mixture of a mineral oil, a vegetable oil and a long-chain aliphatic acid with fuming H_2SO_4 at $\not> 20°$c. and after sulphation and/or sulphonation is completed adding an alkylated phenol, e.g. dibutyl- or diamyl-phenol, to stabilise the product and to act both as a penetrant and as an antioxidant, finally neutralising with alkali metal hydroxide. C. O. C.

Stable Aqueous Dispersions of Cellulose Ethers. American Viscose Corpn. *BP* 714,752

Cellulose ethers dissolved in 0·5–4·0% aq. caustic alkali remain in stable dispersion when the pH is adjusted to pH 5–9 by adding a compound which neutralises the alkali. Such dispersions may be used as sizing, finishing or coating compositions, thickening agents for paints, etc. C. O. C.

Preparation of *N*-2′-(4″-chloro-2″-sulphophenoxy)-5′-chlorophenyl-*N*′-3:4-dichlorophenylcarbamide—Mothproofing Agent. Variapat. *BP* 715,067

The above mothproofing agent is obtained in a very readily soluble form by condensing a salt of 2-amino-4:4′-dichloro-1:1′-diphenylether-2′-sulphonic acid with dichloro-

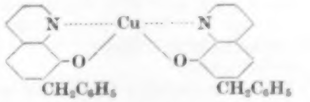
phenyl *iso*cyanate in anhydrous acetonitrile. The product is in two forms, a less soluble one which crystallises out on standing and one which gives a 33·3% soln. in warm water and which remains in solution. The latter product is especially suitable for use in the dyebath as there is little danger of its hydrolysing. C. O. C.

2-Thiocyano-4:6-diamino-*s*-triazine — Mothproofing Agent and Dye Intermediate. American Cyanamid Co. *USP* 2,649,447

2-Thiocyano-4:6-diamino-*s*-triazine, prepared by treating dicyanoguanidine with thiocyanic acid in a menstruum at −10 to 110°c., is a mothproofing agent applicable from solution in acetone. It is also an intermediate in dye manufacture. C. O. C.

Copper 7-Benzyl-8-quinolinate— Mildew Preventative. Bristol Laboratories. *USP* 2,649,451

Copper 7-benzyl-8-hydroxyquinolinate—



formed by treating 7-benzyl-8-hydroxyquinoline with a soluble cupric salt, is useful for the mildewproofing of textiles. C. O. C.

Fire-retardant Composition. N.V. Lak-, Vernis- en Verffabriek Molyn & Co. *BP* 714,809

The fire-retardant properties of coatings based on water-insoluble compounds which release ammonia on heating, e.g. $MgNH_4PO_4·6H_2O$, are considerably improved by addition of inorganic nitrites or nitrates, e.g. $2K_3Co(NO_2)_6·3H_2O$ or $BiONO_3·H_2O$, and/or organic compounds containing a nitro or nitroso group, e.g. nitrourea or nitrosoguanidine. Still further improvement is obtained by adding in addition a water-soluble acid salt which liberates acid on heating, e.g. $MgHPO_4·3H_2O$. C. O. C.

***NN*-Dimethylacetamide as Solvent for Polyacrylonitrile.** DuP *USP* 2,649,427

NN-Dimethylacetamide readily dissolves polyacrylonitrile to yield solutions which are stable when kept for long periods. C. O. C.

Solvents for Acrylonitrile Polymers (VI p. 518).
Solvent for Polyacrylonitrile (VI p. 518).
Stability of Sodium Formaldehyde-sulphoxylate (IX p. 522).

IV—RAW MATERIALS; INTERMEDIATES; COLOURING MATTERS

Production of Intermediates for Azo Pigments and Lakes. D. A. W. Adams. *J. Oil & Col. Chem. Assocn.*, **37**, 443–460 (Aug. 1954).

The economics of intermediate production are briefly treated; depreciation costs are higher than in the dye-making industry, and the introduction of new products may be a costly and lengthy matter. The manufacture of a number of typical intermediates is described in some detail, these being: 3-nitro-*p*-toluidine (M.N.P.T.), from toluene via *p*-toluidine (the *p*-amino group being protected by temporary acetylation or *p*-toluenesulphonation during the nitration stage); *p*-nitroaniline, from acetanilide via *p*-nitroacetanilide, and from *p*-chloronitrobenzene by amination; C acid (6-chloro-*m*-toluidine-4-sulphonic acid) from toluene, by successive sulphonation, chlorination, nitration, isolation of the appropriate chloronitrotoluenesulphonic acid as the Na or Ca salt, and reduction, and from *p*-toluenesulphonyl chloride, by successive chlorination, nitration, hydrolysis, and reduction; Tobias acid (2-aminonaphthalene-1-sulphonic acid), from 2-naphthol by sulphonation followed by Bücherer amination. The production of numerous coupling components is also detailed; these include: 2:3-hydroxynaphthoic acid from 2-naphthol (including two processes recently patented by E. B. Higgins— for which no references are given); various acetoacetarylides, by condensation of amines with ethyl acetoacetate, and from keten by straight addition to amines; *m*-4-xylidine, by isolation as acetate from the mixed xylidine obtained from commercial xylene or, when a high degree of purity is required (e.g. for making dyes for the food industry), from xylene by a controlled sulphonation and desulphonation process which yields *m*-xylene of purity > 95%, which is nitrated and fractionated. J. W. D.

Benzo Fast Copper Dyes and Analogous Products. E. D. G. Frahm. *Chemisch Weekblad*, **48**, (9), 127–131 (1952).

For about 50 years it has been known that the light fastness of certain azo dyes such as Cotton Blue N (Ciba) (dianisidine⇉(1-naphthol-4-sulphonic acid)$_2$, *C.I.*502) and Chicago Blue 6B (FBy) (dianisidine⇉(1-amino-8-naphthol-2:4-disulphonic acid)$_2$, *C.I.*518) can be improved by after-treating with copper salts, but because of the instability on repeated washing of the complexes so formed, the light fastness falls.

Over the last 30 years, a large number of soluble copper-containing dyes have been marketed, such as the following Sirius Supra dyes, the constitutions of which are given in *BIOS* 1548—

Sirius Supra Blue GL (FBy): copper complex of dianisidine⇉(chromotropic acid)$_2$, which is the copper complex of Dianil Blue G, *C.I.*508.

Sirius Supra Blue FBGL (FBy): copper complex of
dianisidine ↗ 1-naphthol-3:8-disulphonic acid
↘ 2-phenylamino-5-naphthol-7-sulphonic acid

Sirius Supra Rubine BBL (FBy): copper complex of (2-anisidine-4-sulphonic acid)$_2$⇉5:5′-dihydroxy-7:7′-disulpho-2:2′-dinaphthylurea.

Sirius Supra Brown BR8 (FBy) = Chlorantine Fast Brown BRLL (Ciba) = Solar Brown PL (8) = Diphenyl Fast Brown BRL (Gy):
benzidine ↗ salicylic acid
↘ (copper complex of 2-aminophenol-4-sulphonic acid→resorcinol).

Such dyes are generally very fast to light but, because of the solubility of the complexes, only moderately fast to washing.

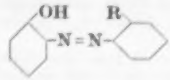
About 1930 the I.G. introduced the Benzo Fast Copper dyes, which are dyed by the usual method for direct cotton dyes and which on aftercoppering in another bath, e.g. with copper sulphate and acetic acid at 70°c. for 30 min., give insoluble copper complexes on the fibre, thus giving dyeings which have good light fastness and good fastness to washing below 70°c. (at higher temp. the complexes are decomposed with a reduction in the fastness to washing). The Coprantine (Ciba) and Cuprophenyl (Gy) dyes are similar to the Benzo Fast Copper dyes. The former can also be dyed by the Coprantine process, in which the dyeings are aftertreated with Coprantine Salt II, which is added to the dyebath after it has been exhausted. Coppering takes place not only with the dye on the fibre but also with that in the dyebath, and so the dyeings are treated with Ultravon W or with soap soln. to remove any loosely attached copper complex, thus improving the fastness to rubbing. This process gives excellent results with dyes which exhaust almost completely, such as Coprantine Blue RLL and 3RLL, Bordeaux BGL, Black Brown 8, and a few others; but large losses of dye occur with dyes of moderate exhaustion, such as Coprantine Yellow Brown GLL, Red 2G, and Navy Blue CBLL and C3RLL, and in such cases it is impossible to use a standing bath. The fastness of these aftercoppered dyeings is generally good. The fastness to acids, especially of many of the Coprantine dyes, is poor, but treatment in a slightly alkaline bath usually restores the original colour. Discharging is difficult under neutral conditions, better results being obtained by a special method under alkaline conditions, cf. *Dutch Patents* 61,668 (Ciba) and 62,958 (Gy).

In many cases formation of the copper complex is accompanied by a considerable change in colour—

Dyes	Colour of the Direct Dyeing	Colour of the Coppered Dyeing
Benzo Fast Copper Yellow RLN	Orange	Brownish yellow
Benzo Fast Copper Brown 3GL	Orange	Yellowish brown
Benzo Fast Copper Red RL	Brownish red	Red
Benzo Fast Copper Violet 3RL	Reddish violet	Bluish violet
Coprantine Brown 5RLL	Brownish orange	Reddish brown
Coprantine Brown 8RLL	Brown	Reddish brown
Coprantine Red BLL	Red	Bluish red
Coprantine Fast Blue 2GLL	Blue	Greenish blue
Coprantine Green 5GLL	Green	Yellowish green
Coprantine Grey 2RLL	Violet	Grey

In other cases, e.g. Cuprophenyl Navy Blue BL and RL, Coprantine Bordeaux BGL, and Benzo Fast Copper Blue FBL, there is only a slight dulling of the colour.

Complex formation in these ranges of dyes occurs mostly by means of a salicylic residue or the grouping—



(R = OH, COOH, O·Alk, O·CH_2·COOH, or a group which readily splits off on treatment with a Cu salt. The following dyes illustrate the various possibilities, the constitutions of the Benzo Fast Copper dyes being given in *BIOS* 1548 and *BIOS Miscellaneous* 20, and those of the Coprantine and Cuprophenyl dyes by reductive scission. The identity of some dyes was established by their colour reactions with acids, alkalis, etc.

(a) Dyes containing Salicylic Residues

Benzo Fast Copper Blue GL (FBy) = Coprantine Blue BLL (Ciba):
p-aminosalicylic acid → 1-naphthylamine-7-sulphonic acid → 1-naphthylamine $\xrightarrow{\text{Alk}}$ 2-amino-5-naphthol-7-sulphonic acid.

Benzo Fast Copper Yellow GRL (FBy) = Sirius Supra Yellow FRRL (FBy):
condensation product of 2 mol. of [3-*p*-aminobenzoylamino-2-hydroxy-5-sulphobenzoic acid → *m*-toluidine] with phosgene.

Coprantine Yellow 2G (Ciba) = Chlorantine Fast Yellow 3G (Ciba) = Neocupran Yellow 3G (Ciba):
presumably a condensation product of phosgene with two different yellow monoazo dyes, one of which contains a salicylic acid residue and the other a sulphosalicylic acid residue (cf. *Swiss Patents* 234,516, 234,518, and 234,520).

Coprantine Green 5GLL (Ciba) = Chlorantine Fast Green 5GLL (Ciba) = Neocupran Green 5GLL (Ciba) = Solophenyl Brilliant Green 5GL (Gy) = Solar Green 5GL (S):
condensation product of 1 mol. of cyanuric chloride with 1 mol. of 1-amino-4-(4-amino-3-sulpho)-anilidoanthraquinone-2-sulphonic acid, 1 mol. of 4′-amino-4-hydroxyazobenzene-3-carboxylic acid, and 1 mol. of aniline (*Swiss Patent* 182,878).

Coprantine Green 3GLL (Ciba) = Chlorantine Fast Green FGLL (Ciba) = Neocupran Green 3GLL (Ciba):
has a composition similar to that of the preceding product, but a *p*-aminobenzoyl residue is inserted between the anthraquinone dye and the triazine ring (*Swiss Patents* 217,241 and 220,647).

(b) Dyes containing *oo*′-Dihydroxy-azo Groups

Benzo Fast Copper Rubine RL (FBy):
(6-chloro-2-aminophenol-4-sulphonic acid)$_2$ $\rightrightarrows$ bis-2-hydroxy-6-naphthoyldianisidine.

Benzo Fast Copper Bordeaux BL (FBy):
(6-nitro-2-aminophenol-4-sulphonic acid)$_2$ $\rightrightarrows$ bis-2-hydroxy-6-naphthoyldianisidine.

Benzo Fast Copper Red RL (FBy):
condensation of 2 mol. of 6-nitro-1-amino-2-naphthol-4-sulphonic acid → 1-*p*-aminophenyl-3-methyl-5-pyrazolone with 1 mol. of phosgene.

Coprantine Pure Blue 2GLL (Ciba):
3:3′-dihydroxybenzidine $\rightrightarrows$ 2 mol. of 2-amino-5-naphthol-7-sulphonic acid.

The properties of dyes from 3:3′-dihydroxybenzidine differ considerably depending on the coupling conditions. Those of Coprantine Pure Blue 2GLL show that the coupling was done in the presence of lime. Coupling in the presence of KOH gives a product with different properties (*Swiss Patent* 246,422).

Coprantine Brown 5RLL (Ciba):
benzidine ↗ salicylic acid
↘ resorcinol ← 2-aminophenol-4-sulphonamide
(*Swiss Patent* 208,538).

(c) Dyes containing *o*-Hydroxy-*o*′-carboxy-azo Groups

Benzo Fast Copper Violet BBL (FBy):
benzidine-3:3′-dicarboxylic acid ↗ 1-naphthol-5-sulphonic acid
↘ 2-phenylamino-5-naphthol-7-sulphonic acid.

Benzo Fast Copper Violet 3RL (FBy):
condensation product of 1 mol. of phosgene with 2 mol. of reduced (2:5-diaminobenzoic acid → 2-phenylamino-5-naphthol-7-sulphonic acid).

Benzo Fast Copper Yellow RLN (FBy):
4:4′-diamino-3:3′-dicarboxydiphenylurea ↗ acetoacetanilide
↘ 1-*m*-sulphophenyl-3-methyl-5-pyrazolone.

Coprantine Bordeaux BGL (Ciba):
benzidine ↗ salicylic acid
↘ 2-amino-5-naphthol-7-sulphonic acid $\xleftarrow{\text{Alk}}$ anthranilic acid.

(d) Dyes containing *o*-Hydroxy-*o*′-alkoxy-azo Groups

Benzo Fast Copper Blue FBL (FBy) = Cuprofix Blue CFBL (S):
benzidine-3·3′-bis-hydroxyacetic acid $\rightrightarrows$ 2 mol. of 2-*p*-methoxybenzoylamino-5-naphthol-7-sulphonic acid.

Benzo Fast Copper Blue F3GL (FBy):
p-aminosalicylic acid → 1-amino-6-sulpho-2-naphthoxyacetic acid → 2-(*p*-benzoylaminophenylamino)-5-naphthol-7-sulphonic acid.

Coprantine Blue GLL (Ciba):
(4-amino-2:5-dimethoxy-4′-hydroxyazobenzene-3′-carboxylic acid)$_2$ $\rightrightarrows$ 5:5′-dihydroxy-7:7′-disulpho-2:2′-dinaphthylamine (*Swiss Patent* 183,684).

Coprantine Blue RLL (Ciba):
(4-amino-2-methyl-5′-methoxy-4′-hydroxyazobenzene-3′-carboxylic acid)$_2$ $\rightrightarrows$ 5:5′-dihydroxy-7:7′-disulpho-2:2′-dinaphthylamine (*Swiss Patent* 187,024).

Coprantine Blue 3RLL (Ciba):
4-amino-2-methyl-5-methoxy-4′-hydroxyazobenzene-3′-carboxylic acid → 5:5′-dihydroxy-7:7′-disulpho-2:2′-dinaphthylamine ← 3-amino-4-methoxytoluene (*Swiss Patent* 227,126).

Coprantine Green G (Ciba):
5-amino-2-hydroxy-3-sulphobenzoic acid → 3-amino-4-methoxytoluene → condensation product of 1 mol. of cyanuric chloride with 1 mol. of 1-amino-8-naphthol-3:6-disulphonic acid, 1 mol. of 4′-amino-4-hydroxyazobenzene-3-carboxylic acid, and 1 mol. of aniline (*Swiss Patent* 221,205).

Cuprophenyl Grey 2BL (Gy):
p-aminosalicylic acid → 1-naphthylamine-7-sulphonic acid → 2:5-dimethoxyaniline $\xrightarrow{\text{Alk}}$ 2-amino-5-naphthol-7-sulphonic acid $\xleftarrow{\text{Acid}}$ 5-nitro-2-aminobenzoic acid (*Swiss Patent* 244,518).

Cuprophenyl Black RL (Gy) = Cuprofix Black R (S):
dianisidine ↗ salicylic acid
↘ 2-amino-5-naphthol-7-sulphonic acid $\xleftarrow{\text{Acid}}$ 5-nitro-2-aminobenzoic acid (*Swiss Patent* 250,815).

Cuprophenyl Navy Blue RL (Gy) = Cuprofix Navy Blue GRL (S) is a similar composition except that the salicylic acid is replaced by a naphthol derivative (*Dutch Patent* 58,536).

More recently, the Neocupran (Ciba) and Cuprofix (S) ranges have been marketed. These are given a slightly different aftertreatment, since with only a few products, such as Neocupran Yellow 3G, Green 3GLL and 5GLL, and Cuprofix Blue CFBL, Navy Blue GRL, and Black R, are insoluble complexes formed with copper sulphate and acetic acid, thus giving the desired improvement in fastness to washing. The Neocupran dyeings are aftertreated at room temp. with Neocupran F, which is a mixture of Lyofix SB, copper and ammonium salts, and sodium

carbonate (*Swiss Patents* 247,682 and 253,632). The Lyofix SB forms an insoluble compound with the dye, as it does with many other direct cotton dyes, thus improving the fastness to water and washing. Dyeings of the Cuprofix range are aftertreated with Cuprofix S New at room temp. or preferably at 70°C. Some of the dyes in these ranges do not form copper complexes, and in some cases are themselves soluble copper complexes, e.g.—

Neocupran Blue RL (Ciba) = Chlorantine Fast Blue GLL (Ciba) = Diphenyl Fast Blue GLN (Gy) = Solar Blue G (S) = Sirius Fast Blue BRR (FBy):

2-naphthylamine-4:8-disulphonic acid → 1-naphthylamine → 1-naphthylamine-7-sulphonic acid $\xrightarrow{\text{Alk}}$ 2-amino-5-naphthol-7-sulphonic acid.

Cuprofix Orange 2GL (S) = Solar Orange 2GL (S) = Neocupran Orange 3GLL (Ciba) = Chlorantine Fast Orange 3GLL (Ciba) = Sirius Supra Orange GGL (FBy): condensation product of 1 mol. of 4:4′-dinitrostilbene-2:2′-disulphonic acid with 1 mol. of 4-aminoazobenzene-4′-sulphonic acid of which the nitro group has been reduced to the amino.

Neocupran Violet 5BLL (Ciba) = Chlorantine Fast Violet 5BLL (Ciba) = Cuprofix Violet 2BL (S) = Solar Violet BL (S) = Solophenyl Violet 4BL (Gy):
copper complex of (2-aminophenol-4-sulphonamide)$_2$ ⇉ 5:5′-dihydroxy-7:7′-disulpho-2:2′-dinaphthylamine (*Swiss Patent* 81,396).

In fastness properties these two ranges of dyes resemble the aftercopperable ranges already mentioned, except that in some cases the fastness to washing, especially above 60°C., and the fastness to light are lower than those of the corresponding Chlorantine and Solar dyes, owing to the presence of Lyofix SB and of a product of similar properties in the Cuprofix S New, e.g. Neocupran Red BNLL (Ciba) = Chlorantine Fast Scarlet BNLL (Ciba), Neocupran Blue 3GLL (Ciba) = Chlorantine Fast Blue 3GLL (Ciba), Neocupran Blue RL (Ciba), Cuprofix Orange 2GL, Grey 4GL, Blue Green B (S), and others. Some products further possess poor acid fastness, and discharging is often difficult or impossible. In some cases there is also a considerable change in colour on aftertreatment, e.g. Neocupran Red 2R = Cuprofix Red 5BL, and Neocupran Red BNLL. Some of the Neocupran and Cuprofix dyes are identical with those in other ranges of direct cotton dyes. For Neocuprans the identity is given by Ciba in the relevant pattern card For the Cuprofix dyes, this can be shown by colour reactions with acids and alkalis, e.g.—

Cuprofix Rubinole BL (S) = Solar Rubinole B (S) = Neocupran Violet 2RLL (Ciba) = Chlorantine Fast Violet 2RLL (Ciba) = Solophenyl Violet 2RL (Gy)

Cuprofix Brown GL (S) = Solar Brown PL (S) = Neocupran Brown BRLL (Ciba) = Chlorantine Fast Brown BRLL (Ciba) = Diphenyl Fast Brown BRL (Gy) = Sirius Supra Brown BRS (FBy)

Cuprofix Black Brown 2BL (S) = Neocupran Dark Brown B (Ciba) = Cupranil Dark Brown B (Ciba) = Benzo Chrome Brown B (FBy)

Cuprofix Black C (S) = Viscose Black NF extra (S) = Neocupran Black CA (Ciba) = Artificial Silk Black CA (Ciba) = Cotonerol AB Extra (FBy)

Cuprofix Grey 4GL (S) = Solar Grey 4GL (S) = Neocupran Grey 3GLL (Ciba) = Chlorantine Fast Grey 3GLL (Ciba)

Cuprofix Red 5BL (S) = Chloramine Copper Red 5BL (S) = Neocupran Red 2R (Ciba) = Chlorantine Red 2R (Ciba)

Cuprofix Blue 2GL (S) = Solar Blue 2GLN (S)

Cuprofix Blue 3GL (S) = Solar Blue 3GLN (S).

Cuprofix Blue 4GL (S) = Solar Blue F (S)

C. H. R.

New Types of Thermochromic Substances. The Stereochemical Aspect of Thermochroism; Thermochroism and Vinylogy. A. Schönberg, A. Mustafa and W. Asker. *J. Amer. Chem. Soc.*, **76**, 4134–6 (20 Aug. 1954).

Some compounds, e.g. rubrene, and anthraquinone mono-*p*-dimethylaminoanil, in inert solvent solution show marked changes in colour on being heated. This is explained by the following hypothesis: In overcrowded molecules in which planarity is hindered, the degree of non-planarity changes with temperature. This is associated with change of colour, one reason being that resonance is related to planarity. If the molecules absorb in the visible region, thermochroism may be observed with the naked eye.

C. O. C.

Absorption and Fluorescence of Crystal Violet, Methyl Violet and Malachite Green. E. Laffitte and Y. Dubreuil. *Compt. rend.*, **238**, 787–9 (1954): *Chem. Abs.*, **48**, 8651 (10 Aug. 1954).

The metallic model theory allows the recovery with good approximation of the maximum ultraviolet absorption bands from the measured frequencies of the visible bands. In its usual form, however, this theory does not enable determination of the value p_0 for those molecules whose electronic symmetry eliminates *a priori* the hypothesis of a unique linear oscillator. C. O. C.

Colours of Indigoids. T. Nakajima. **I.** *Science Reports, Tohoku Univ.*, **37**, 257–263 (1953): **II.** *Ibid.*, 264–274: *Chem. Abs.*, **48**, 8651 (10 Aug. 1954).

I—The absorption bands of indigo, dihydroindigo and thioindigo were calculated by the linear combination atomic orbitals molecular orbital method. Because simplifying assumptions lead to ambiguities in the parameters involved, the calculated transitions lie at longer wavelengths than those observed.

II—The method was extended with simplifying modifications to 5:5′- and 6:6′-dinitro-, *NN*- and 7:7′-dimethyl, 5:5′- and 7:7′-dimethoxy- and 1:1′-diacetyl indigo, *iso*indigo and indirubin. Blue shifts are produced in the substituted indigos because of the non-alternant skeleton of indigo and the hetero atoms it contains. The calculated and observed values despite additional simplification of the method of calculation are closer than with indigo (but still not exact) because of fortuitous cancellation of opposing divergent effects. C. O. C.

Syntheses of Cyanine Dyes. XV—A New Method of Synthesising Brooker-type Neocyanine. Y. Tanabe. *J. Pharm. Soc. Japan*, **73**, 855–860 (1953); **XVI—Synthesis of Asymmetric Brooker-type Dyes containing Two Different Heterocyclic Nuclei.** *Ibid.*, 860–7. **XVII—A New Method of Synthesising Asymmetric Trinuclear Dyes containing Three Different Heterocyclic Rings.** *Ibid.*, 972–6: *Chem. Abs.*, **48**, 8093–6 (25 July 1954).

Dye Phosphors. V—Pre-excitation Effect of the Dye Phosphors. D. Yamamoto. *J. Chem. Soc. Japan*, Pure Chem. Sect., **75**, 512–521 (1954): *Chem. Abs.*, **48**, 8057 (25 July 1954).

Study of the pre-excitation effect of dye phosphors having trypaflavine, Acridine Yellow, Acridine Orange or Crystal Violet as phosphorescent centres showed that a negative effect is obtained when citric acid, succinic acid, "glassy" glucose, gelatin or filter paper is used as the base. Trypaflavine or Acridine Yellow have positive effect when surface-adsorbed in high concentration. As negative pre-excitation effect is parallel to the decolorisation of the dyes it is deemed to be caused by their photodecomposition. The positive pre-excitation effect seems to be related to the state of polymerisation or aggregation of the dye molecules.

C. O. C.

Organic Phosphors having Metallic Compounds as the Phosphorescent Bodies. I—Crystals of Metallic Salts suitable for the Phosphorescent Bodies and the Effects of Metallic Ions on the Phosphorescent Colour. R. Iwaki. *J. Chem. Soc. Japan*, Pure Chem. Sect., **75**, 524–530 (1954): *Chem. Abs.*, **48**, 8057 (25 July 1954).

Investigation of the phosphorescence shown by 24 dyes dissolved in 150 metallic salts shows that azo dyes are non-phosphorescent. Metaborates are good phosphorescent bases for di- and tri-phenylmethane and acridine dyes, and chlorides and nitrates for xanthen dyes. With such solutions abnormal colour is shown by acridine dyes when Ca^{++} and Pb^{++} are present. This abnormal colour is not caused by β-phosphorescence, as the life of phosphorescence, even in the long wave range, is affected by temperature. Seemingly the abnormal colour is caused by a solvent effect or formation of dye–metal complexes. "Monochloroacetate"

is a good phosphorescent base. With organic phosphorescent bases abnormal colour is caused with acridine dyes by presence of Ag^{+}, Hg^{++}, and Pb^{++} and with acid xanthen dyes by Sr^{++}, Ag^{+} and Pb^{++}. C. O. C.

Phthalocyanines. H. Wahl. *Teintex*, **19**, 589–602 (Aug. 1954).

A review with a short bibliography. S. R. C.

Blue Phthalocyanine Pigments. II—Colours with Copper, Iron or their Metallic Compounds. M. Mori. *J. Chem. Soc. Japan*, Ind. Chem. Sect., **56**, 116–8 (1953): *Chem. Abs.*, **48**, 8555 (25 July 1954).

Phthalocyanine pigments were made according to Wyler's method using urea (26 g.), H_3BO_3 (1), phthalic anhydride (20) and 2–11 g. of Cu, CuCl, CuO, $Cu(NO_3)_2$, Cu acetate, Fe, $FeCl_2$, $FeCl_3$, $FeSO_4$, Fe_2O_3 and $K_3Fe(CN)_6$ and heating at 220–250°C. for 2–4 hr. With Cu coppers the resulting pigments were violet–blue and the yields $< 58\%$. With iron compounds the pigments were too dark and there were low yields. C. O. C.

Cyanine Dyes. IX—Syntheses of Oxonol and *mero*-Cyanine Dyes. H. Zenno. *J. Pharm. Soc. Japan*, **73**, 1063–6 (1953); **X—Syntheses of Intermediates of Oxonol Dyes.** *Ibid.*, 1066–8: *Chem. Abs.*, **48**, 8543 (25 July 1954).

IX—Syntheses of products such as bis(barbituric acid)-5-methinoxonal (a yellow dye), bis(3-ethylrhodanine)-5-methinoxonal (a red dye), 2-(barbitur-5-ylidene-ethylidene)-1-methyl-1:2-dihydroquinoline (an orange dye), etc. are given.

X—Syntheses of products such as (*p*-methoxyanilinomethylene)barbituric acid are given. C. O. C.

Anthraquinone Vat Dyes. K. J Bradley and P. Kronowitt. *Ind. Eng. Chem.*, **46**, 1146–1156 (June 1954).

The manufacture of anthraquinone vat dyes is illustrated by a detailed description of the commercial preparation of Cibanone Brown BR by fusion of 1:4-diaminoanthraquinone with 1-chloroanthraquinone. The methods of manufacture of the intermediates from *p*-chlorophenol and phthalic anhydride, and from anthraquinone, respectively, are also described. W. K. R.

Biosynthesis of Chlorophyll Pigments. K. Egle. *Naturwissenschaften*, **40**, 569–576 (1953): *Chem. Abs.*, **48**, 8877 (10 Aug. 1954).

Review of syntheses of chlorophyll in the plant, protochlorophyll, basic building bricks for porphyrins, and the phyllogeny of pyrrole pigments. Many references. C. O. C.

Chlorophyll. III—Chromatographic Investigations on Chlorophyll. T. Vrbaški. *Arhiv Kem.*, **23**, 184–7 (1951): *Chem. Abs.*, **48**, 8291 (25 July 1954).

Vrbaški has previously shown that aromatic nitro and nitroso compounds form compounds or complexes with chlorophyll *in vitro* and that these compounds are stable to light and do not fluoresce. He now shows that the same type of compound is formed if the chlorophyll is in the adsorbed state (on sucrose). C. O. C.

Polarographic Behaviour of Juglone. P. Zuman. *Chem. Listy*, **48**, 524–532 (1954): *Chem. Abs.*, **48**, 8675 (10 Aug. 1954).

Juglone shows a reversible polarographic wave preceded by an adsorption fore wave. In presence of H_3BO_3 at pH > 6 complex formation occurs, a new wave forms, and stability to hydrolysis increases. C. O. C.

Melanin Formation, Existence of 5:6-Dihydroxyindoles as Essential Intermediate Products during the Enzymic Oxidation of Tyrosine, Dihydroxyphenylalanine, and Adrenaline. D. Kertész. *Bull. Soc. chim. biol.*, **35**, 1157–1165 (1953): *Chem. Abs.*, **48**, 8278 (25 July 1954).

Formation of 5:6-dihydroxyindole and 2-carboxy-5:6-dihydroxyindole from the red oxidation products of dihydroxyphenylalanine is catalysed by Zn compounds and is not inhibited by cyanide. Further oxidation to melanin can be catalysed by a polyphenol oxidase, this reaction being accelerated by traces of Cu. These two dihydroxyindoles do not seem to be formed during enzymic conversion of adrenaline to melanin. C. O. C.

Pseudohypericin, a New Red Hypericum Pigment. H. Brockmann and W. Sanne. *Naturwissenschaften*, **40**, 461 (1953): *Chem. Abs.*, **48**, 8333 (25 July 1954).

Hypericin preparations from 14 species of *Hypericum*, in all but one case (*H. hirsutum*), showed hypsochrome shift of the absorption bands over 15 mμ. with intensified red fluorescence when their green solutions in H_2SO_4 were irradiated. Evidently only the hypericin from *H. hirsutum* is true 4:5:7:4′:5′:7′-hexahydroxy-2:2′-dimethyl-*meso*-naphthodianthrone. The other 13 preparations contain pseudohypericin. The conversion product obtained by irradiation is a derivative of *meso*-anthrodianthrene: hence the pseudohypericin has in 2:2′ positions substituents which can cyclise to a new benzene ring. The conversion product has unknown substituents in the new benzene ring. The yellow, crystalline benzoates obtained from the 13 pseudohypericins have not sharp m.p., indicating that they are the derivatives of mixtures. C. O. C.

Carbon Blacks for Protective Coatings. I—Manufacture and General Properties. L. J. Venuto. *Paint*, **24**, 197–202 (June 1954).

A review of the history of the manufacture, types, properties and testing of carbon blacks. C. O. C.

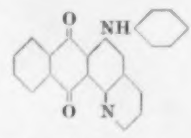
Pink Pigments of MnO–P_2O_5–Al_2O_3 and Cr_2O_3–P_2O_5–Al_2O_3 Systems. G. Yamaguchi and K. Tomiura, *J. Ceram. Assoc. Japan*, **62**, 111–4 (1954): *Chem. Abs.*, **48**, 8507 (25 July 1954).

Mixtures of $MnHPO_4 \cdot 3H_2O$ and $Al(OH)_3$ calcined at 1100°C. yielded a pink pigment when $Al_2O_3 : MnO :: 3:4$. The colour was caused by an amorphous substance which surrounded α-Al_2O_3 crystals. Formation of Mn spinel turned the product brown. Mixtures of $CrPO_4$ and $Al(OH)_3$ or $AlPO_4$ calcined at 1300–1400°C. yielded a violet–pink pigment when $Al_2O_3 : Cr_2O_3$ was < 6. C. O. C.

PATENTS

1-Phenylamino-3:4(*N*)-pyridinoanthraquinones—Disperse Dyes. Celanese Corpn. of America. *BP* 713,153

1-Amino-4-hydroxyanthraquinone is subjected to a Skraup synthesis and the resulting hydroxypyridinoanthraquinone in the form of its leuco compound condensed with aniline or one of its nuclear-substituted derivatives. The products are blue disperse dyes of good gas fume fastness when dyed on cellulose acetate rayon. Thus the dye—



is prepared by first heating 1-amino-4-hydroxyanthraquinone with glycerol, H_2SO_4 and nitrobenzene at 100–120°C. for 6 hr.; the product is reduced to its leuco form by treating with alkaline $Na_2S_2O_4$, refluxed with alcoholic aniline containing H_3BO_3, and finally aerated. R. K. F.

Chloromethylated Vat Dyes. General Aniline. *USP* 2,645,645

Arylamino-anthanthrones, -dibenzpyrenequinones and -pyranthrones are treated with dichlorodimethyl ether to form chloromethyl derivatives, which are convertible to the corresponding water-soluble onium salts, and which produce the corresponding methyl derivatives on the fibre after vatting. Thus di(*p*-toluidino)anthanthrone in H_2SO_4 is heated at 60°C. for 16 hr. with dichlorodimethyl ether and the product separated by pouring into ice and water.

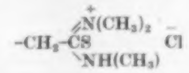
USP 2,645,646

Chloromethylated dibenzanthronyls, dibenzanthrones and *iso*dibenzanthrones are prepared similarly. R. K. F.

Thiouronium Derivatives of Dibenzanthronyl, etc. General Aniline. *USP* 2,619,492

Soluble thiouronium salts of dibenzanthronyl, dibenzanthrone and *iso*dibenzanthrone are prepared by treating their chloromethylated derivatives with a thiourea or a tertiary amine. Thus bischloromethyldibenzanthrone is

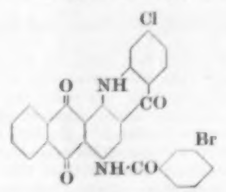
refluxed for 30 min. with aq. 1:1:3-trimethylthiourea and poured into acetone after cooling. The water-soluble product containing the groups—



dyes cotton, wool and silk directly violet or may be paste-printed and developed by vat or acid ageing methods.
R. K. F.

Cobalt Complexes for Printing. FBy. *BP* 713,459
The method described in *BP* 687,655 (J.S.D.C., **69**, 217, (1953)) is improved to increase the amount of yellow-brown cobalt complex useful for printing, by adding NH_4NO_3 to the reaction mixture. Thus phthalic anhydride, urea, anhyd. cobalt chloride, NH_4NO_3 and ammonium molybdate are heated together in nitrobenzene at 160–180°C.
R. K. F.

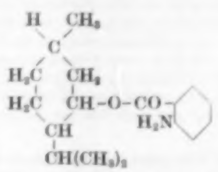
Phthaloylacridone Vat Dyes. CFM. *BP* 713,512
An *o*- or *m*-halogenobenzoyl chloride is condensed with 3-amino-8-chloro-1:2-phthaloylacridone to produce red-blue vat dyes which are greener and stronger than those obtained by using *p*-halogenobenzoyl chloride as in *BP* **633,132** (J.S.D.C., **66**, 301 (1950)). Thus the dye—



is prepared by heating 3-amino-8-chloro-1:2-phthaloylacridone with 3-bromobenzoyl chloride in *o*-dichlorobenzene at 160°C. for 12 hr.
R. K. F.

Phthalocyanine Chrome Dyes. FBy. *BP* 713,397
The *o*-hydroxycarboxylic acid combination is introduced into phthalocyanines by condensing a phthalocyanine containing $Cl{\cdot}SO_2$-groups, and a benzenesulphonyl group also carrying a $Cl{\cdot}SO_2$- group, with an aromatic amino-*o*-hydroxycarboxylic acid or its ester, to form dyes which chrome to clear green-blues, when printed on cellulose. Thus the phthalocyanine prepared from diphenylsulphone-3:4-dicarboxylic imide and phthalic anhydride is heated at 90–95°C. for 3 hr. with chlorosulphonic acid and thionyl chloride. After separating by pouring into ice and water, the resulting chlorosulphonyl compound is stirred at room temperature with aq. 2-hydroxy-5-amino-3-sulphobenzoic acid and $NaHCO_3$.
R. K. F.

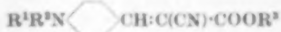
Menthyl Anthranilate as a Fluorescent Identifying Agent for Use in Photographic Elements. Kodak and Kodak-Pathé S.A. Française. *BP* 715,580
Incorporation of very small amounts of menthyl anthranilate—



into the film base of a photographic material results in purplish fluorescence on exposure to ultraviolet radiation. The fluorescence has no effect on the emulsion layer.
C. O. C.

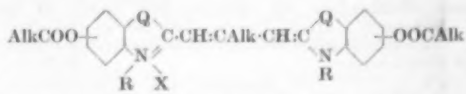
7-Diethylamino-4-methylcoumarin as a Fluorescent Identifying Agent for Use in Photographic Elements. Eastman Kodak Co. *USP* 2,649,375
0·001–0·002% on the weight of a cellulose ester film of 7-diethylamino-4-methylcoumarin results in a purplish fluorescence being shown under ultraviolet radiation. This fluorescence has negligible effect on light-sensitive layers and may be incorporated in them.
C. O. C.

Methin Dyes. General Aniline. *USP* 2,649,471
Dyes of formula—



(R^1, R^2 and R^3 = same or different Alk) are obtained economically in excellent yield by condensing a suitable *p*-dialkylaminobenzaldehyde with an appropriate cyanoacetic acid alkyl ester in absence of an inert solvent at a temperature which keeps the product liquid until condensation is complete, using piperidine or a similar compound as catalyst. The products have at least as good fastness and dyeing properties as the products obtained by the previously known solvent process of manufacture and in some cases yield brighter dyeings.
C. O. C.

Symmetrical *meso*-Alkylacyloxycarbocyanine Dyes. Kodak. *BP* 715,256
Dyes of formula—



(R = subst. or unsubst. Alk or alkylene; Q = O or S; X = anion) are produced by condensing a hydroxy-2-methylbenzthiazole or a hydroxy-2-methylbenzoxazole quaternary salt with an orthoalkylcarboxylic acid ester in presence of an aliphatic carboxylic acid anhydride. They have photographic sensitising properties. C. O. C.

Highly Dispersed Vat Dye Preparations. Basf. *BP* 714,825
When precipitating vat acids from alkaline vats of vat dyes in presence of dispersing agents, very fine homogeneous dispersions are obtained if the precipitation is done in a sound field, preferably one of frequency > 1000 hertz.
C. O. C.

Highly Dispersed Vat Dye Powders. CFM. *BP* 714,964
The dye is reduced and then reoxidised while kneading it with a water-soluble plastic. This results in a product which forms a colloidal solution in water in which the degree of dispersion of the dye is finer than is obtained by the processes of *BP* 485,466 (J.S.D.C., **54**, 438 (1938)) and *USP* 1,892,280.
C. O. C.

Sulphur-containing Carbon Black. Deutsche Gold- und Silber-Scheideanstalt vormals Roessler. *BP* 715,184
Carbon blacks is heated to 150–350°C. with sulphur, a solution of sulphur or a compound giving up sulphur at this temperature. Furnace and light lampblacks take up 6–7% of sulphur, heavy lampblacks take up 2–3%. The product is a useful filler for rubber as it helps in vulcanising, seemingly because the sulphur forms a bridge between the rubber molecule and the filler; it is also useful for making black lacquers.
C. O. C.

Modified Carbon Blacks. Deutsche Gold- und Silber-Scheideanstalt vormals Roessler. *BP* 715,185
Modified carbon blacks containing a desired radical, e.g. S, CN, OH or OC_6H_5, are produced by heating a halogenated carbon black with a compound containing the desired radical.
C. O. C.

Metallic Oxides produced by Oxidation or Hydrolysis of Volatile Metallic Halides. DuP. *BP* 715,255
A method of producing e.g. TiO_2 in which the scaly oxide deposits are removed and their formation is controlled so that it does not interfere with but promotes the oxidation or hydrolysis reaction.
C. O. C.

Titanium Dioxide. British Titan Products Co. *BP* 714,857
Titanium dioxide of high tinting strength is produced by roasting a mixture of mineral rutile and an alkali-metal compound so that they are not fused, and lixiviating with water to remove impurities. The alkali titanate left is boiled with aqueous $\geqslant$ 32% HCl or H_2SO_4 and the resulting TiO_2 calcined at 500–1000°C.
C. O. C.

2-Thiocyano-4:6-diamino-*s*-triazine— Mothproofing Agent and Dye Intermediate (III p. 511).
Classification of Aluminium Pigments (V p. 516).
Pigment for Anti-fouling Paint (V p. 516).

A Study of Certain Natural Dyes. II—The Structure of the Metallic Lakes of the Brazilwood and Logwood Colouring Matters (VIII p. 519).
Printing and Dyeing with Azoic Dye Compositions (IX p. 522).
Improving Stability to Ultraviolet Radiation (XIII p. 525).
Benzidine Rearrangement during Titration of Azo Compounds with Titanous Chloride (XIV p. 526).

V—PAINTS; ENAMELS; INKS

Classification of Aluminium Pigments. G. M. Babcock and F. B. Rethwisch. *Paint, Oil & Chem. Rev.*, **117**, (7), 37–9, 46–8 (1954): *Chem. Abs.*, **48**, 9709 (25 Aug. 1954).

Review of the manufacture, characteristics, selection of type of pigment and vehicle, application and storage of aluminium paints. C. O. C.

Some Reflections on Twenty-five Years of Ink Research. R. F. Bowles. *J. Oil & Col. Chem. Assocn.*, **37**, 461–470 (Aug. 1954).

A broad review. J. W. D.

PATENTS

Stabilised Black Stencil Ink. Marsh Stencil Machine Co. *USP* 2,649,381

An ink which gives a good solid black and does not tend to settle out on long standing consists of asphaltum, gloss oil (e.g. a limed rosin, 50% mineral spirits by weight), carbon black, soyabean lecithin, and Stanolex (Standard Oil Co.). C. O. C.

Pigment for Anti-fouling Paint. Minister of National Defence of Canada. *BP* 715,535

Copper powder or flake milled with graphite so as to embed the graphite in the copper when used in paints has a leaching rate several times that of copper powder alone and in addition the leaching rate tends to increase during the early period of leaching. C. O. C.

Improving Stability to Ultraviolet Radiation (XIII p. 525).
Colour Master Batches of Plastics, Rubber, Resins, Waxes, Gums, etc. (XIII p. 525).

VI—FIBRES; YARNS; FABRICS

Effects and Dispersal of Electrostatic Charges on Fibres. A. Sippel. *Melliand Textilber.*, **35**, 831–835 (Aug. 1954).

Static may be prevented by mixing fibres which acquire positive and negative charges, and by selecting suitable constructional materials for machinery. Antistatic products and ionisation of the atmosphere are discussed. S. R. C.

Pentoses associated with Jute α-Cellulose. D. B. Das, M. K. Mitra, and J. F. Wareham. *Nature*, **174**, 228–229 (31 July 1954).

The criticisms of Sarkar and co-workers regarding the presence of pentoses in jute α-cellulose and the use of the formic acid method of hydrolysis are discussed. Chromatograms are given supporting the presence of pentoses in jute α-cellulose. W. R. M.

Chemical Changes and Incrustation of Viscose Rayon Staple Textiles during Wear. T. N. Kleinert, V. Mössmer, and W. Wincor. *Textil-Rund.*, **9**, 393–395 (Aug. 1954).

Shirts made of viscose rayon staple and repeatedly worn and washed were examined for chemical degradation and ash content. Apart from physical effects, such as splitting of fibre-ends, the degree of polymerisation decreased and the number of carboxyl groups and the amount of ash increased. H. E. N.

Cellulose Acetate as a Raw Material for Rayon Production. A. R. Urquhart. *J. Appl. Chem.*, **4**, 195–203 (April 1954).

A brief account of the development of the process for making acetone-soluble "secondary" cellulose acetate is given. Early applications are outlined, and solubility characteristics briefly discussed. The advantages of cellulose acetate rayon, its subjective qualities, competition from synthetic-polymer fibres, and possible changes in structure are discussed. W. R. M.

Deformation of Hair and Wool Keratin in Solutions of Organic Compounds. A. G. Pasynskii and V. P. Blokhina. *Khim. i Fiz.-Khim. Vysokomolekul. Soedinenii, Doklady 7-oi Konf. Vysokomolekul. Soedineniyam*, 291–297 (1952): *Chem. Abs.*, **48**, 8547 (25 July 1954).

Measurements of tensile strength, the relative size of the hysteresis ring, and of the temperature dependence of strain of hair and wool keratin in solutions of urea, urethan, detergents, salt buffers and Na dithionite show that in solutions of buffers, urea, guanidine, urethan and detergents weakening of intermolecular interaction (salt, H and non-polar bonds) leads to decrease in tensile strength and increase in the elastic properties. Rupture of the disulphide bonds by dithionite decreases both tensile strength and elastic properties. C. O. C.

Theory of Diffusion of Sorbed Substances into and out of Fibres. B. Olofsson. *Discussions Faraday Soc.*, (16), 34–45 (1954).

The relation between the equilibrium sorption isotherm and the sorption-coupled diffusion for fibres is discussed. For a finite bath, exact solutions to the diffusion equations can be obtained by introducing certain linear approximations to the sorption isotherm. Theoretical curves agree with those obtained experimentally for sorption of HBr on wool. Practical applications of the theory are summarised. W. R. M.

Absorption of Sodium Sulphate and Sulphuric Acid by Hair. D. L. Underwood and H. J. White. *Discussions Faraday Soc.*, (16), 66–75 (1954).

Equilibrium and rate measurements of absorption of H_2SO_4 and Na_2SO_4 by hair are made by a radioactive tracer method. Results agree with those obtained by conventional titration methods. Na_2SO_4 is found to be absorbed in appreciable quantities in a manner suggesting adsorption on bonding sites within the fibre. Some absorption and desorption studies on single fibres are described. W. R. M.

Selective Absorption of Optical Antipodes by Wool. W. Bradley, R. A. Brindley, and G. C. Easty. *Discussions Faraday Soc.*, (16), 152–158 (1954).

Wool immersed in aqueous (±)-mandelic acid absorbs the (+) form more abundantly than the (−) form. Mandelic acid is similarly resolved by combination with L-arginine and L-lysine. Since these are the principal basic amino acids of wool, it seems probable that mandelic acid combines with wool. A number of derivatives of mandelic acid and certain related molecules are also resolved. About 75% of the equilibrium amount of bound acid combines within 4 min., and resolution occurs from the beginning of the process. *p*-Hexadecoxymandelic acid is not resolved. Some derivatives, in contrast to mandelic acid itself, are retained by wool after immersion in water. W. R. M.

Chemical Denaturation of Groundnut Protein and Fibre Formation. W. E. F. Naismith. *J. Appl. Chem.*, **4**, 188–194 (April 1954).

Two types of denaturing agents—(*a*) urea, guanidine salts, and related compounds; and (*b*) amines—are investigated with groundnut protein for fibre formation. The considerable rise in the viscosity increment of the protein on denaturation with urea and the hydrochloride and thiocyanate of guanidine, and with bases of dissociation constant $> 10^{-4}$, is interpreted in terms of increased asymmetry of the protein molecules. Only where such a rise is observed can solutions of the protein with the denaturant be prepared suitable for extrusion into fibre. W. R. M.

Crystallisation Phenomena in Fibre-forming Polymers. L. B. Morgan. *J. Appl. Chem.*, **4**, 160–172 (April 1954).

The mechanism by which long chain molecules order themselves into some form of crystalline array is postulated to be one involving normal nucleation processes, modified to take into account the facts that polymers melt over a range of temp. and that the nucleation act is followed by preferential crystal growth in the direction of the polymer chains. This mechanism, with the additional concept of coiling growth, is not inconsistent with kinetics which fit the crystallisation rate process on the one hand and the observable structure of crystalline polymers on the other. It is considered that lateral accretion of the polymer

molecules to already formed long helical polymer crystals results in haphazard branching growth with the new fibril developing along a path parallel to the parent crystal. This leads to the formation of coiled families of fibrillar crystals, and this structure appears to explain X-ray observations made at various stages of the drawing and relaxing of filaments of crystalline polymers. W. R. M.

Shape and Surface Structure of Synthetic Fibres. J. A. Chapman and J. W. Menter. *Chem. and Ind.*, 1012 (14 Aug. 1954).

The advantages of the electron microscope over the optical microscope in the examination of the curved surfaces of fibres are briefly discussed. The effect of wear on fibres has been studied. The nature and the extent of the damage depend on the type of fibre and the load applied. With light loads damage is confined to smooth surface scratches, but at high loads severe tearing of the surface occurs, with bulk deformation of the whole fibre. W. R. M.

Production of Fibres from 6,6-, 6,10-, and 6-Polyamides. G. Meacock. *J. Appl. Chem.*, **4**, 172–177 (April 1954).

Differences in physical and chemical properties of 6,6-, 6,10-, and 6-polyamides are reflected in the conditions required for the production of fibres and in their properties. These factors are compared. The 6,6-polymer has the highest m.p. and the lowest thermal stability. The 6-polymer produces a fibre containing sufficient monomer to involve process complications and its initial modulus is low. The 6,10-fibres absorb less moisture than the 6,6 or the 6. W. R. M.

Drawing of Terylene. J. Marshall and A. B. Thompson. *J. Appl. Chem.*, **4**, 145–153 (April 1954).

A method of analysis of continuous drawing processes in terms of the basic load–extension–temperature properties is given. Experimental work is largely confined to polyethylene terephthalate (Terylene multifilament yarn), for which quantitative results are given. These include load–extension curves covering the temp. range in which uniform extension occurs and results on "natural" draw ratios when the extension proceeds by "necking". A brief account of a theory of cold-drawing is given, and the results are discussed in the light of this theory. W. R. M.

Static Electrification of Synthetic Fibres. E. Darmois. *Chem. and Ind.*, 1012 (14 Aug. 1954).

Fibres of Rhovyl (polyvinyl chloride—P.V.C.), Rhovylon (82% P.V.C. + 18% nylon), and Rhovylane (25% P.V.C. + 75% wool) were rubbed with a number of different materials, and the charge acquired was measured with a Faraday cylinder. Pure P.V.C. was always negatively charged. The following triboelectric series was established— silk (positive), wool, glass, metals, resins, ebonite, P.V.C. (negative). Fabrics made from mixtures containing wool were positively charged, but no charge was acquired with fabrics made from 25% P.V.C. and 75% wool. Loss of static charge from fabrics made from synthetic fibres was measured under standard conditions after the fabrics electrified by friction had stood for 30 min. in atmospheres of controlled humidity. Fabrics of Rhovyl retained their charge almost completely in atmospheres of up to 80% R.H. Dacron, Orlon, dynel, and Acrilan completely lost their charge after 30 min. in atmospheres of R.H. > 65%. A theory of static electrification is developed in which it is suggested that during rubbing electrons are released which, in the case of P.V.C. fibres, are fixed by their affinity for Cl atoms. W. R. M.

Extrusion and Properties of Saran Monofilaments. J. Jack and R. A. Horsley. *J. Appl. Chem.*, **4**, 178–188 (April 1954).

Manufacturing details of the production of Saran (vinylidene chloride copolymer) monofilaments are given. Changes in molecular structure occurring during each stage of the production are analysed, and the effects of these on the properties of the final monofilament are discussed with a view to obtaining conditions for producing monofilaments with optimum properties. W. R. M.

Polyaminotriazoles as Fibre-forming Materials. J. W. Fisher. *J. Appl. Chem.*, **4**, 212–219 (April 1954).

A new series of condensation polymers, the polyaminotriazoles, are described. These are most simply made by condensation of aliphatic dihydrazides in the presence of excess of hydrazine. The polymers are fibre-forming and can be melt-spun to give filaments which, after drawing, possess high strength and good affinity for dyes of the acid and disperse types, as used for cellulose acetate rayon. W. R. M.

PATENTS

Degumming Vegetable Fibres. Société D'Exploitation des Procédés Lourd, S.E.P.L. *BP* 713,342

Vegetable fibres, e.g. flax, hemp, and jute, which have been chemically retted and are still coated with a sheath of pectic substances and hemicelluloses in the form of colloids, are treated with a 0·001–1·0% aqueous solution of a surface-active agent of the sulphated oil and sulphonated fatty acid type so as to reduce interfacial tension between the aqueous and colloidal phases, and then with a 0·2–2·0% aqueous acid (the strength varying inversely with the dissociation constant) to flocculate and precipitate the colloids, which are finally removed by rinsing. J. W. B.

Dispersing Agents for Viscose. Phrix-Werke. *BP* 712,707

Addition of organic sulphonic acid esters of alkanolamines of general formula $(R^1SO_2OR^2)_2NR^2OH$ (R^1 = alkaryl; R^2 = alkyl) to viscose prevents clogging of the spinnerets and increases the extensibility of the yarn. By means of these compounds it is also possible to disperse animalising agents of various types in viscose so that the resulting rayon can be dyed with wool dyes. W. G. C.

Highly Adsorbent and Water-absorbent Artificial Fibres. F. D. Timmermans. *BP* 712,683

Absorbent fibres, e.g. those used in bandage-like materials, are prepared by extruding spinning solutions containing finely divided activated charcoal which has been treated with emulsifiers stable to alkali. The amount of activated charcoal is such that 10% of 0·01% aq. Methylene Blue will be absorbed in 30 min. W. G. C.

Fire-retardant Cellulose and Cellulose Ether Fibres, Films, etc. Monsanto. *BP* 714,214

Addition of the neutral to alkaline reaction product of phosphorus oxychloride and ammonia to aqueous solutions of cellulose, cellulose xanthate or a cellulose ether, imparts fire-retardant and afterglow-resistant properties to dry coagulates prepared from such solutions. C. O. C.

Wet Treatment of a Tow of Filaments or Threads in Absence of Tension. ICI. *BP* 715,206

The tow is heated with a liquid of greater sp.gr. than the filaments by introducing the tow by means of a current of the liquid through a tubular structure into a tube leading therefrom. The tube inclines upwards in the direction of flow and is wider than the narrowest part of the tubular structure. An appreciable length of the upper internal surface of the tube is below the free surface of the heating liquor in it. The tow is withdrawn continuously from the outflowing liquid after an interval of time such that a quantity of lapped tow collects against the upper internal surface of the tube, and so that each portion of the tow remains in the treating liquor for the necessary period. Withdrawal of some of the liquor near the inlet end of the tube diminishes the speed of the liquor through the tube and improves the regularity of the lapped tow below the free surface of the liquor. C. O. C.

Stabilising Synthetic Linear Polyamides to Heat. DuP. *BP* 715,364

Incorporation of 0·1–1·0% of phosphorous acid and 0·25–2·5% of an alkali metal halide, e.g. KBr or KI, stabilises nylon, etc. to heat and oxygen. C. O. C.

Fibres of Grafted Acrylonitrile Polymers or Copolymers. ICI. *BP* 715,194

Fibres of enhanced affinity for dye compared with previously known polyacrylonitrile fibres are made from "grafted" polyacrylonitrile, i.e. polymers consisting of one or more chains of acrylonitrile, if desired with a small proportion of other vinyl compounds, attached chemically to a polymeric molecule of different chemical composition, e.g. the product obtained by polymerising acrylonitrile in presence of 5–40% by wt. of a water-soluble organic compound containing the CH bond and of mol. wt. > 1000. C. O. C.

Solvents for Acrylonitrile Polymers. BrC. *BP* 712,983

Polyacrylonitrile may be dissolved at < 80°c. in a mixture of nitromethane (50% by wt.) and compounds containing two or more phenolic hydroxyl groups, e.g. catechol or resorcinol. The solutions remain liquid at the temperature of formation.

BP 712,986

Acrylonitrile polymers can in general be dissolved in or swollen by mixtures of polyhydric phenols with organic compounds of mol. wt. greater than that of nitromethane which have themselves some solvent or swelling action on polacrylonitrile, e.g. dicarboxylic acids of 2–5 C or nitrosamines.

BP 712,990

Acrylonitrile polymers can be dissolved in anhydrous formic acid, aqueous formic acid of ≮ 70% concentration, mixtures of these with other solvents for polyacrylonitrile, or an aqueous mixture of formic and oxalic acids.

BP 712,994

Nitrosodiphenylamine, preferably alone but if desired diluted to some extent with a compound (except a dihydric phenol) which has no swelling or solvent action, is a good solvent for polyacrylonitrile.

BP 712,998

Anhydrous mixtures of nitromethane and carboxylic acids of > 1C and dissociation constant 1×10^{-4} and 2×10^{-5} or their aqueous mixtures of dissociation constant $2{\cdot}25 \times 10^{-5}$ and 2×10^{-3} are particularly useful solvents for producing spinning solutions of acrylonitrile polymers, especially those which are insoluble in acetone.

BP 712,999

Mixtures of nitromethane with lactones of hydroxy-fatty acids, alkylene cyclic carbonates, cyclic anhydrides of saturated aliphatic dicarboxylic acids, β-nitro- and β-cyano-ethanols, nitro- and cyano-substituted higher homologues of ethanol containing a polar substituent atom or group for each C atom in excess of two in the nitro- or cyano-substituted alkanol, and unsaturated aliphatic acids of dissociation constant 2×10^{-3} at 25°c., or an anhydrous mixture of nitromethane (< 50% by wt.) and a cyclic anhydride of an unsaturated aliphatic dicarboxylic acid have greater solvent power for polyacrylonitrile than the components by themselves.

BP 713,000

Aqueous mixtures of nitromethane, formic and/or oxalic acid are useful solvents for polyacrylonitrile.

BP 713,049

Nitrosamines of > 2C and stable up to 120°c. are solvents for acrylonitrile polymers. C. O. C.

Solvent for Polyacrylonitrile. Courtaulds. *BP* 714,530

A solution containing water, an aliphatic liquid of < 7C and containing an alcoholic hydroxyl group, the proportion of water to aliphatic liquid being from 2 : 1 to 1 : 4, and ≮ 35% (on the total wt. of soln.) of an alkaline earth thiocyanate, ammonium or guanidine thiocyanate, lithium bromide or iodide, sodium iodide or zinc chloride, is a good solvent for polyacrylonitrile polymers. C. O. C.

Solutions of Polyacrylonitrile. Chemstrand Corpn. *BP* 715,232

The viscosity of solutions of polyacrylonitrile in *NN*-dimethylacetamide containing 2–8% of acetic acid is reduced so that it can be used as a spinning solution by addition of 0·05–0·25% of sulphuric or sulphamic acid. C. O. C.

Acrylonitrile–Acrylamide Copolymers having High Affinity for Acid Dyes. Industrial Rayon Corpn. *USP* 2,649,438

Copolymers of acrylonitrile and a water-soluble *N*-morpholinoethylacrylamide sulphate or an acrylamide of formula—

$$H_2C{:}CR{\cdot}CO{\cdot}NR\begin{cases}A{\cdot}N'XY\\Z\end{cases}$$

(R = H or Alk of < 3C; A = alkylene of > 1C or arylene; N′ = *tert.* N; X and Y taken singly = Alk, hydroxyalkyl, cyanoalkyl, *cyclo*alkyl, aralkyl or Ar; X and Y taken jointly = a divalent radical forming a heterocycle with N′; Z = subst. or unsubst. pyridyl radical; the amide N atom is linked to Z by a pyridyl ring C atom), e.g. $CH_2{:}CH{\cdot}CO{\cdot}NH{\cdot}CH_2CH_2N(CH_3)_2$, are readily formed into oriented fibres, etc. having very high affinity for acid dyes. C. O. C.

Dipping, Stretching, Compressing, Drying and Winding Rovings and Yarn. Dan River Mills. *USP* 2,649,071

A machine in which several rovings or yarns are passed into a liquid, untwisted, twisted, compressed, squeezed, partly dried, compressed, dried, set and packed. After being squeezed the materials are kept under the same tension throughout the remaining operations. The method is particularly suitable for treating yarn with binding material so as to obtain fine-count yarns of high tensile strength without use of high tension. C. O. C.

Flow through Textile Filter Media (VIII p. 519).
Significance of Hydrogen Bonding in Textile Chemistry (VIII p. 519).
Kinetics of Absorption of Water and Aqueous Solutes by Dry Viscose Cellulose (VIII p. 519).
Kinetics of Acid Absorption on Wool Fibres (VIII p. 520).
Combination of Acids and Dye Acids with Keratin (VIII p. 520).
Colour Master Batches of Plastics, Rubber, Resins, Waxes, Gums, etc. (XIII p. 525).
Filament Surface Investigation by a Simple Interferometric Method with particular reference to Nylon Filaments (XIV p. 527).

VII—DESIZING; SCOURING; CARBONISING; BLEACHING

Theory and Practice of Enzymatic Desizing. J. Voss. *Melliand Textilber.*, **35**, 762–764 (July), 876–880 (Aug. 1954).

Investigations of the effects of time, temperature, and pH on the quantity of residual starch after bacterial, pancreatic, and malt desizing are described. Storage and temperature stability increase in the presence of calcium salts, silicates, thioformamide, and sodium dihydrogen phosphate. Rapid, continuous, and full-width desizing processes are discussed, together with the use of J-boxes and heated zones. S. R. C.

Relation of Molecular Structure to Detergency of Some Alkylbenzenesulphonates. F. N. Baumgartner. *Ind. Eng. Chem.*, **46**, 1349–1352 (June 1954).

Laboratory washing tests carried out on an isomeric series of sodium alkyl(C_{12})benzenesulphonates have shown that detergency reaches a maximum when the benzene ring is attached to the third alkyl C atom. The critical micelle concentration increases as the benzene ring is moved towards the centre of the alkyl chain. The effect of added sodium sulphate on detergency depends more on solubility than on structure, being most beneficial for the more soluble products. With two homologous series in which the benzene ring was attached to the third and fourth C atoms of a linear alkyl chain, the best performance was on average obtained with a C_{12} chain, for the products of higher mol. wt. were more sensitive to hard water. In contrast, wetting power was greatest when the benzene ring was at the centre of the alkyl chain. W. K. R.

Mode of Action of Detergents. H. L. Rosano. *Teintex*, **19**, 577–587 (Aug. 1954).

The tensiometric technique of J. and L. P. Guastalla was used to study wetting phenomena, and the behaviour of oil drops on a solid surface immersed in water and in detergent solution was observed. The mechanical work involved in detergency is that of emulsification or intermicellary solution, and is reduced by the effect of the detergent on the oil–water interfacial tension. The physical action of the detergent is limited, as a measurable residue of soil is left, which is removed only by the chemical action of mineral salts used as builders. The sign of the ionic charge of the detergent is of importance in the redeposition of emulsified oil. S. R. C.

Cotton Finishing Developments (X p. 523).
Shrinkage in Laundering of Cotton and Rayon Fabrics (XIV p. 527).

VIII—DYEING

Flow through Textile Filter Media. G. E. Cunningham, G. Broughton, and R. R. Kraybill. *Ind. Eng. Chem.*, **46**, 1196–1200 (June 1954).

The resistance of felted materials to the flow of air is represented by the equation—

$$-\Delta P = k\eta v$$

($-\Delta P$ = pressure drop in in. of water; η = viscosity of the fluid in centipoises; v = superficial velocity in ft./min.; and k = constant dependent on the fabric = approx. 0·03 × wt. in oz./sq.yd.). Woven fabrics obey the equation at low velocities, but there is marked deviation at high rates of flow owing to turbulence. The flow of water and oils was in general represented by the equation, but oils gave increased and water gave greatly increased values of k. These differences are considered to be due to wetting effects and aeration. The addition of a wetting agent to water greatly increased the flow resistance. W. K. R.

Physical Chemistry of Dyeing and Tanning—General Introduction. E. K. Rideal. *Discussions Faraday Soc.*, (16), 9–13 (1954).

Mechanisms operative in dyeing are discussed and the importance of rate of stirring is emphasised. W. R. M.

Significance of Hydrogen Bonding in Textile Chemistry. W. Happe. *Melliand Textilber.*, **35**, 871–876 (Aug. 1954).

The significance of hydrogen bonding in fibre structure (cellulose, polyamide, and polyacrylonitrile) and dyeing processes (dyeing of wool and acetate rayon, application of vat, direct, and azoic dyes) is briefly discussed. The rôles of polyglycol ethers and polyvinylpyrrolidone in vat dyeing, and the swelling of cellulose are examined. S. R. C.

Adsorption of Dyes by Crystals. J. Whetstone. *Discussions Faraday Soc.*, (16), 132–140 (1954).

The importance of dye adsorption in crystal habit modification phenomena is confirmed. Adsorption is not necessarily on the habit-modified plane. More frequently, it is perpendicular to the modified face of the crystal, which is very reasonable if modern views on layerwise growth processes of crystal faces are accepted. Evidence is obtained in support of the view that adsorption is due to a close similarity in pattern between polar groups of dye molecule and the ions of a crystal plane. The type of crystal plane involved depends on the nature of the dye molecule. W. R. M.

A Study of Certain Natural Dyes. I—The Adsorption of Brazilwood and Logwood Colouring Matters by Fibres. F. M. Arshid, J. N. Desai, D. J. Duff, C. H. Giles, S. K. Jain, and I. R. Macneal. J.S.D.C., **70**, 392–401 (Sept. 1954).

The adsorption properties of haematein, the colouring matter from logwood, and its leuco compound, haematoxylin, together with brazilein, the colouring matter from brazilwood, have been studied on several types of fibre. Brazilein and haematein are weak acids and are adsorbed by wool or nylon appreciably only from acid solutions, probably by hydrogen bonding between the fibre and the undissociated haematin or brazilein molecules, as well as by acid–base combination with the charged amino groups in the fibre. The adsorption of haematoxylin by cellulose acetate, nylon, and wool is most probably attributable to the formation of hydrogen bonds with the fibre, those formed by nylon and wool being stronger than those formed by cellulose acetate. The adsorption by cellulose appears to be of a different nature and to be attributable to weaker forces, probably van der Waals attraction.

Some evidence is given that haematoxylin may act as a cross-linking agent between the peptide groups in the molecular chains of proteins.

Analytical methods for the colouring matters are evaluated. Refractometry was used in determining the adsorption of haematoxylin. A simple and effective method of packing loose fibres for adsorption tests is described. AUTHORS

A Study of Certain Natural Dyes. II—The Structure of the Metallic Lakes of the Brazilwood and Logwood Colouring Matters. F. M. Arshid, R. F. Connelly, J. N. Desai, R. G. Fulton, C. H. Giles, and J. C. Kefalas. J.S.D.C., **70**, 402–412 (Sept. 1954).

The lake-forming reactions of the oxidised and reduced forms of the logwood and brazilwood colouring matters with the more important mordanting metals have been investigated. The oxidised forms appear to be the lake-forming species, the *o*-hydroxyquinone system of the molecule chelating with the mordanting metal atom; the leuco forms must first be oxidised by air or the mordanting salt before lake formation can take place. When a chromate or a dichromate is used as mordant, this is first reduced to the chromic cation, at the expense of the total destruction of some of the colouring matter, before lake formation occurs.

The logwood colouring matter, when treated with a chromium salt in solution or on the fibre, forms a deep blue 2:1 (dye : metal) complex, which is preceded by a transient purple 1 : 1 complex. Aluminium, cobalt, and (ferric) iron also form 2 : 1 complexes, and copper appears to form a 1 : 1 complex.

The lakes formed in substance are amorphous, infusible, and almost insoluble in all solvents.

The deep blue–black logwood lake on the fibre is believed to be a mixture of an anionic complex, e.g. $[hnCr(OH)_2hn]^-[Cr(OH)_2(H_2O)_4]^+,4H_2O$ with the derived olated body—

$8H_2O$ (hn = Haematein anion)

The iron lake is probably similar in constitution.

In addition to the action of the chelating groups, the phenolic groups not in the quinonoid nucleus of the colouring matter molecule appear to take part also in salt formation with cobalt or copper, but not with chromium or iron. AUTHORS

Atomic Models. III—Some Stereochemical Problems in Dyeing. C. Robinson. *Discussions Faraday Soc.*, (16), 125–132 (1954).

The use of Hartley–Robinson models in the study of stereochemical problems in dyeing is discussed with particular reference to cellulose and polypeptide chains. The anisotropic flexibility of the cellulose chain is shown, and it is suggested that, contrary to the usual assumptions, hydrogen bonding to cellulose can occur irrespective of the positions of hydrogen-bonding groups in the dye molecule. When an amide group links two aromatic rings together, it seems unlikely that the group can be in the *cis* position when attached to cellulose. The possible part played by steric hindrance in the dyeing of a synthetic polypeptide is discussed. W. R. M.

Researches on Monolayers. IV—Study of Dyeing Processes by Use of the Unimolecular Film Balance. M. M. Allingham, C. H. Giles, and E. L. Neustädter. *Discussions Faraday Soc.*, (16), 92–105 (1954).

Possible modes of dye–fibre association are studied by a surface balance method, interpretation of interaction being based on measurements of molecular area and compressibility. Model compounds of low mol. wt. are used to represent typical fibres. There is evidence for the formation of CH . . . N and CH . . . O intermolecular bonds in cellulose acetate–dye and Terylene–dye systems. In cellulose–dye systems association may be due to van der Waals attraction. In the dyeing of proteins and nylon, some evidence for intermolecular hydrogen bonds is obtained, but this does not always agree with data from sorption experiments. W. R. M.

Kinetics of Absorption of Water and Aqueous Solutes by Dry Viscose Cellulose. H. B. Mann and T. H. Morton. *Discussions Faraday Soc.*, (16), 75–84 (1954).

Kinetics of wetting of single viscose filaments by aqueous solutions of simple solutes and a dye and the subsequent absorption of solute on the filament are studied. Wetting is complete in ca. 10 sec. at 20°C. Rate of wetting is approx. proportional to surface area, and the temperature

coefficient corresponds to an activation energy of ca. 7 kcal. per mole. Simple inorganic salts, urea, glycerol and sucrose are taken up by the fibre proportionately rather more slowly than water. Absorption of a direct cotton dye on wetting the fibre in aqueous solution follows a different course. Very little dye is absorbed during wetting, the dye presumably being concentrated at the interface; thereafter redistribution of dye occurs by well known diffusion mechanisms. W. R. M.

Colour Changes of Vat Dyeings during Soaping. J. Wegmann; E. Kornreich. J.S.D.C., **70**, 412–413 (Sept. 1954).

Discussion of the molecular and crystallisation theories of the colour changes. C. J. W. H.

Theoretical Aspects of the Dyeing of Cellulose Acetate Rayon. C. L. Bird, F. Manchester, and P. Harris. *Discussions Faraday Soc.*, (16), 85–92 (1954).

The aqueous solubility of a number of disperse dyes is determined, and some are found to be appreciably soluble at 80°C. Even the most insoluble are solubilised to some extent by dispersing agent added to the dyebath, and in such cases the rate of dyeing of cellulose acetate rayon is increased. The available evidence is considered to support Clavel's view that dyeing takes place from a dilute, saturated aqueous solution. A study of the equilibrium distribution between fibre and dyebath of one of the more soluble disperse dyes shows a linear partition resembling that of a solute between two immiscible solvents. W. R. M.

Solubility and Activity of Orange II in Sodium Chloride and Sodium Sulphate Solutions. A. B. Meggy. *Discussions Faraday Soc.*, (16), 149–152 (1954).

The solubility of Orange II in NaCl and Na_2SO_4 solutions at 25°C. has been determined and the activity factor calculated. The partition of the dye between amyl alcohol and water, 0·05N-NaCl, and 0·2N-NaCl has been studied, but the data do not permit determination of k in the activity factor ky. The activity coefficient increases by a factor of 30–50 in 2N-NaCl or 2N-Na_2SO_4, and is sufficient to nullify the stripping and levelling effects of these electrolytes at higher temp. The behaviour of certain cellulose acetate dyes towards salts can be explained on the assumption that they show the same type of behaviour at 80–100°C. as Orange II at 25°C. W. R. M.

Kinetics of Acid Absorption on Wool Fibres. R. F. Hudson. *Discussions Faraday Soc.* (16), 14–24 (1954).

Kinetics of adsorption of acids on wool initially in the isoelectric state are studied, acid concn., temp., degree of agitation, and acid anion being varied. Variation of rate with time is quantitatively interpreted by assuming diffusion of acid through the fibre, followed by adsorption on specific sites, to be rate-determining. Diffusion is found to be controlled by a small concentration of H^+ in the water within the fibres, which may be estimated from Donnan membrane theory. The activation energy for this process is similar to that for diffusion in aqueous solution and for diffusion of water through the swollen fibre. In ion exchange and dyeing, where the rate is controlled by the coupled diffusion of two ions in opposite directions, high activation energies, attributed to deformation of polymer chains, are observed. In acid sorption, swelling reduces the energy required for migration through the fibre. W. R. M.

Combination of Acids and Dye Acids with Keratin. L. Peters and G. H. Lister. *Discussions Faraday Soc.*, (16), 24–34 (1954).

Effects of temp. and concn. on the equilibrium with and diffusion into wool keratin fibres of HCl and the free acid of Orange II are studied. The entropy term is found to provide the major contribution to both equilibrium free energy of desorption and the activation free energy of diffusion in the temp. range 60–100°C. This is attributed to the effect of the solvent (H_2O), whose negative affinity for the dye accounts for the fibre having a large positive affinity and whose hydration of polar groups adds to the diffusion barrier. W. R. M.

Self-diffusion of a Dye in a Polar Polymer Membrane. M. L. Wright. *Discussions Faraday Soc.*, (16), 58–65 (1954).

The equilibrium diffusion coefficient of the anion of Orange II in a membrane of horn keratin is measured by introducing some dye labelled with ^{35}S to a membrane in equilibrium with unlabelled dye. Estimates of H^+ mobility are made and confirmed qualitatively by membrane potential experiments. Dye anion mobility is found to be much smaller than that of H^+ and to vary strongly with concentration. W. R. M.

Calorimetric Studies of the Reaction of Naphthalene Orange G with Amino Acids. A. N. Derbyshire and W. J. Marshall. *Discussions Faraday Soc.*, (16), 140–148 (1954).

Heats of reaction ΔH of eight amino acids with HCl and the free acid of Naphthalene Orange G respectively have been measured. All were found to be $<$ 1 kcal./mole. ΔH was found to be the same for the reaction of any one amino acid with HCl and with the dye acid in every case except that of L-lysine, for which ΔH differed by a few hundred cal. for the two reactions. This is interpreted as evidence that the heat of adsorption of Naphthalene Orange G by wool (ca. 8 kcal./mole) is not due to direct interaction between the groupings in the amino acids and the dye. An extraordinarily high heat of dilution was found for the dye, and it is suggested that this substantiates Meggy's suggestion that the heat of dyeing is due to withdrawal of the large hydrocarbon residue of the dye from the aqueous phase. W. R. M.

Structure of Macromolecular Substances. III—Dyeing of Polyamide Fibre with Acid Dyes. E. K. Mankash and A. B. Pakshver. *J. Appl. Chem. U.S.S.R.*, **26**, 976–981 (Sept. 1953). **IV—Absorption of Naphthylaminesulphonic Acids by Polyamide Fibre.** G. A. Myagkova, A. B. Pakshver, and S. S. Frolov. *Ibid.*, **26**, 991–995 (Sept. 1953). **V—Effect of pH on the Dyeing of Polyamide Fibre.** E. K. Mankash and A. B. Pakshver. *Ibid.*, **26**, 1200–1204 (Nov. 1953).

By use of the diffusion equation discussed in previous communications (see J.S.D.C., **70**, 31 (Jan. 1954)), values of diffusion coefficients for the dyeing of 66-nylon with Durazol Blue 2R (ICI) and Duranol Brilliant Blue BN (ICI) are calculated from data obtained from the results of Munden and Palmer (*J. Textile Inst.*, **41**, P609 (1950)) relating to the dependence of the dyeing properties of the fibre on the amount of cold drawing to which it has been subjected. Also, on the assumption that in Munden and Palmer's experiments on equilibrium uptake of dye one molecule of dye is taken up by each polyamide chain-molecule, the molecular weight of the nylon is calculated from the results for Solway Blue BNS (ICI) (*C.I.*1054) and Naphthalene Scarlet 4RS (*C.I.*185) dyed on undrawn and drawn fibres; the values so obtained ($\sim$27,000) vary only slightly with the degree of draft. The kinetic and equilibrium data so obtained are now supplemented by the results of similar experiments on polyamide fibre [presumably Capron, i.e. 6-nylon] with Direct Blue FF (*C.I.*518) and Cyanol Extra (*C.I.*715), and the results confirm the general conclusions of Munden and Palmer, which are stated to be (i) that the rate of dyeing depends greatly on the degree of draft of the fibre, whereas (ii) the limiting equilibrium uptake of dye is identical for drawn and undrawn fibre. It is stated that Munden and Palmer give no explanation of these facts, and the effect of the change in internal structure on diffusion within the fibre (the rate-determining process) is advanced in explanation of (i), an extension to polyamide fibres of the Poraĭ-Koshits theory of stoichiometric combination of dyes with protein fibres being proposed in explanation of (ii) (it is considered that not only acid dyes, but also disperse dyes, are probably covered by this theory). The ratio of the diffusion coefficients for undrawn and drawn fibres is suggested as an index of the level-dyeing character of the dye [presumably, with respect to irregular yarn], and the effect of the nature of the dye on this ratio and on the value of the diffusion coefficient is discussed. In further work, the absorption of 1-naphthylamine-5-sulphonic acid by drawn and undrawn polyamide fibre at low pH (combination with terminal NH_2 groups) and at high pH (combination with terminal COOH groups) is determined at various temperatures, residual naphthylaminesulphonic acid in solution being coupled with a diazo compound and estimated colorimetrically. The limiting equilibrium absorption for both drawn and undrawn fibre is 5·15 millimoles per 100 g. of fibre at pH 2, 3, and 11. The molecular weight of the polymer calculated from this result is 19,500, which is

regarded as high, since it is considered that not all the end-groups are free to enter into combination with the naphthylaminesulphonic acid. It is nevertheless considered that satisfactory molecular weight determinations can be made by the aid of this principle, and the use of pure Methyl Orange or benzoic acid is proposed for this purpose. The diffusion coefficient is extremely low in neutral solution, and rises in acid and alkaline solution; it is related to the degree of draft in the way already described for dyeing experiments (above). Similar experiments are carried out with Cyanol Extra (pH 2, 3, 4; 30°, 40°, 50°c.). Emphasis is laid on the significance of the apparent activation energy of diffusion, and values calculated from the present results and those of various workers for various fibres are tabulated and shown to be of the same order in all cases. At pH 1 absorption of naphthylaminesulphonic acid and Cyanol Extra continually increases without attaining equilibrium. It is stated that such behaviour has been observed previously by Elöd and Fröhlich (*Melliand Textilber.*, **30**, 103, 239 (1949)), who offered no satisfactory explanation of the phenomenon. The explanation of the increased dye absorption at low pH as being due to combination of dye with amide groupings— the work of Carlene, Fern, and Vickerstaff (J.S.D.C., **63**, 388 (1947)) is cited— is dismissed as improbable. The authors now suggest that hydrolysis of the polymer (which, they have shown, occurs under these conditions) is responsible for the increased absorption at $pH < 2$. A. E. S.

Dyeing of Synthetic Polypeptides. C. H. Bamford, J. Boulton, W. E. Hanby, and J. S. Ward. *Discussions Faraday Soc.*, (16), 222–229 (1954).

A study of the dyeing of a number of synthetic polypeptides suggests that sites in the backbone, side-chains, and amino end-groups may be involved. Conditions affecting dyeing of these groups of sites are discussed. There is no evidence of any difference in the take-up of dye by polymers in the α- and β-configurations. W. R. M.

Mechanism of Absorption of Non-ionic Dyes by Polyethylene Terephthalate. M. J. Schuler and W. R. Remington. *Discussions Faraday Soc.*, (16), 201–209 (1954).

Isotherms are obtained for the distribution of three non-ionic dyes and their binary mixtures between polyethylene terephthalate and water. In each case the equilibrium concn. of dye in the fibre is proportional to the concn. in water. Dissimilar dyes in a binary mixture behave independently, but similar dyes interact slightly. Solubilities of dye in both fibre and water increase with temperature, and the isotherm is displaced toward the water. The presence of benzoic acid displaces all isotherms toward the water. It is concluded that sorption occurs by a solution mechanism. W. R. M.

Dyeing of Polyacrylonitrile Fibres with Anionic Dyes. R. H. Blaker, S. M. Katz, J. F. Laucius, W. R. Remington, and H. E. Schroeder. *Discussions Faraday Soc.*, (16), 210–222 (1954).

The mechanism of dyeing is discussed for two cases in which the fibre, through its affinity for H^+ and Cu^+ respectively, acquires cationic centres permitting absorption of dye anions. Affinity for H^+ is created by basic sites introduced in copolymerisation, and dyeing reactions are interpreted in terms of sites of differing basicity. Every cyano group in polyacrylonitrile seems capable of absorbing cuprous copper through formation of a complex of the type $(RCN)Cu^+$, which acts as a site for fixation of dye anions. W. R. M.

Affinities of the Most Important Dye Groups for Paper Fibres. K. Kletzl. *Wochenbl. Papierfabrik*, **78**, 337–344 (1950): *Chem. Abs.*, **48**, 9690 (25 Aug. 1954).

Dyeing of paper pulp (equal parts of cellulose and mechanical pulp) by acid and basic dyes is an adsorptive process at concentrations of < 18% dye and also at higher concentrations when dyeing is prolonged. Affinity for basic dyes is higher than that for acid dyes. The adsorption isotherm is not followed in the case of direct dyes which are, for the most part, chemically combined. With mechanical wood pulp direct dyes are also chemically combined even where dyeing is slight because of presence of incrustations. The adsorption process is reversible, so that washing the dyed pulp with water removes some of the dye and establishes a new equilibrium. This loss of colour can be avoided by using back water containing some of the dye. C. O. C.

Theory of Leather Dyeing. VI— Study of the Reactions between Aromatic Compounds and Proteins. G. Otto. *Leder*, **5**, 61–4 (1954): *Chem. Abs.*, **48**, 9094 (10 Aug. 1954).

In systems of conjugated double bonds there is increased electron mobility and formation of dipoles and H bridges. Penetration of dyes into leather is not a function of molecular size but depends on total dissociation. Sirius Supra Yellow RT with a chain of 17 conjugated double bonds has great affinity for leather but very poor penetration. Some dyes with many conjugated double bonds do not follow the rule, but examination reveals that the system is broken by an isolating group so that the electron cloud cannot oscillate over the whole molecule. Isolating groups may be CH_2, O, NH, S, or *meta* instead of *para* substitution in the benzene ring. The greater electron mobility that results in chromophoric activity causes the coordinate affinity between dye and fibre. Isolating groups in the dye lower affinity but increase penetration. This was shown by tests with Sirius Supra Brown RL mol. wt. 687 with a system of 11 conjugated double bonds, Acid Leather Brown EGB, mol. wt. 703, with two systems each of 6 conjugated double bonds and Diamine Fast Brown GB, mol. wt. 896, with an NH isolating group between systems of 5 and 8 conjugated double bonds. All had solubility limits at pH 1·3–1·4 and approximately the same gross dissociation as the latter is measured approximately by the lowest pH value at which an anionic dye is completely soluble. The lengths of dyed material in chromatographic columns of hide fibres were 22, 63 and 58 for the dyes in the above order, corresponding values on paper fibre were 19, 81 and 30. Relative penetrations into chrome leather were 2, 5 and 5 respectively. C. O. C.

Practical Colour Matching on Anodic Films. A. E. Bratt. *Bull. Inst. Metal Finishing*, **4**, 63–76 (Spring 1954).

The anodising reaction (and through it the subsequent dyeing process) may be affected by the nature of the alloy used. The processes of anodising and washing-off are briefly discussed; excessive amounts of electrolyte must not be carried forward into the dyebath. The selection and the dissolution of suitable dyes (most of which are wool dyes) are described; a wide choice is not available if colour and fastness requirements are stringent. There is a lengthy discussion of appropriate methods of dyeing, and of the factors involved, e.g. dye-liquor ratio, time, and temp. Where possible, only dyes which form Al lakes should be used; those which are merely adsorbed should be avoided, since they lead to uncontrolled variations during the sealing process. Suitably slow rates of dyeing are ensured by maintaining a pH of 5·2–6·2 by means of an acetate buffer. Single-dye liquors are preferable when practicable, and if mixtures must be used it is essential to discard the dye liquor frequently; procedures for colour matching with two- and three-colour baths are described. The sealing process, in which the anodic film pores are blocked with insol. hydroxide by treatment with steam under pressure, or with vigorously boiling water, is discussed at some length. Reference is made to the meeting of light-fastness requirements in colour matches. J. W. D.

PATENTS

Improving the Fastness to Washing of Materials dyed with Sulphur or Vat Dyes. CFM. *BP* 715,532

Treatment with a solution containing a peralkylated polyalkylenepolyamine, e.g. ethyleneimine polymer permethylated with dimethyl sulphate, and a sulphonic acid of an aromatic nitro compound, e.g. sodium *m*-nitrobenzenesulphonate, increases the fastness to washing of sulphur- and vat-dyed materials even in presence of reducing sizes, e.g. dextrin. C. O. C.

Dyeing Nylon with Azoic Dyes. ICI. *BP* 712,414

The nylon is treated with an aqueous liquor containing an arylamide of a hydroxycarboxylic acid and a compound containing a chain of three N atoms and no free carboxylic or sulphonic acid group and which is obtained by combining a diazotised arylamine with a primary or secondary amine, followed by developing the dye by treatment with hot aqueous mineral acid. C. O. C.

Azoic Dyeing of Nylon and Acetate Rayon. General Aniline. *USP* 2,649,353

Good depth of dyeing, brightness and excellent fastness properties are obtained when applying azoic dyes to nylon or acetate rayon by impregnating the fibres with the necessary azoic coupling components and then diazotising to effect coupling if a guanidine compound is present in the impregnating liquor. The guanidine compound forms a salt with the azoic coupling component, which salt has greater affinity for the fibres than either the coupling component or its sodium salt, it also imparts greater stability to the diazonium compound than the corresponding sodium salt and finally it exerts a buffering action leading to more even and brilliant dyeings. C. O. C.

Dyeing Polyacrylonitrile with Acid Dyes. Chemstrand Corpn. *BP* 713,884

Replacement of sulphuric by nitric acid gives deeper dyeings and better penetration. Much less nitric acid than sulphuric acid is required and the temperature of dyeing may be somewhat lower. The fastness of the dyeings is at least equal to that obtained by use of sulphuric acid. C. O. C.

Benzo Fast Copper Dyes and Analogous Products (IV p. 511).
Pigment Printing and Dyeing (IX this page).
Printing and Dyeing with Azoic Dye Compositions (IX this page).
Cotton Finishing Developments (X p. 523).
Mucoid Material in Hides and Skins and its Significance in Tanning and Dyeing (XII p. 525).

IX—PRINTING

Electrodeposition and the Printing Trade. J. Riley. *Bull. Inst. Metal Finishing*, **4**, 47–62 (Spring 1954).

The three main groups of printing process—relief, lithographic, and intaglio—are briefly described; there is a full account of the preparation and processing of plates and rollers for these methods, with special reference to electrodeposition processes such as that of the chromium facing of rollers. J. W. D.

Thickeners for Printing Azoic Combinations. J. Häusermann. *Textil-Rund.*, **9**, 395–399 (Aug. 1954).

The use of Meypro-Gum CR (Meypro AG, Weinfelden), a non-reducing thickener based on modified carubin, is advocated in conjunction with D-sorbitol as complexing agent for copper. Recipes for typical pastes for screen and roller printing are given. H. E. N.

Stability of Sodium Formaldehyde-sulphoxylate. A. Janson and W. Küppers. *Melliand Textilber.*, **35**, 880–885 (Aug. 1954).

Fe, Cu, Mn, Co, and Ni ions catalyse atmospheric decomposition of Rongalite, the effect being increased by rise in temperature and humidity. Compounds capable of forming complexes with these ions, e.g. citric acid and NaCN, increase the stability of discharge pastes and prints, and enhance the tinctorial value of illuminations. S. R. C.

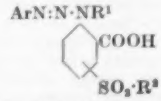
Pigment Printing and Dyeing. G. Bertolina. *Dyer*, **111**, 991–999 (25 June 1954).

Water-in-oil (Aridye, Sherdye, Andotex, Impralac) and oil-in-water (Aquaprint, Aquabond, Aulabrite, Helizarin, Orema, Printofix, Rototex, Sherdye Aqua, Sherdye Padding Colours) compositions, an aqueous solution type (Pigmentweiss C), and the Acramins are compared for printing and overall coloration. Advantages of oil-in-water and aqueous solution types are—lower flammability, miscibility with water (easier dilution and greater ease of cleaning apparatus), and better rubbing fastness on hydrophilic materials. Water-in-oil types, however, yield more stable printing pastes and require a lower solvent : water ratio. Discharge, resist, flock, and metallic powder printing are discussed, and combined pigment dyeing–crease-resisting and pigment dyeing–waterproofing are described. It is stated, however, that hard hand rubbing fastness of pigment compositions is not of the same level as that obtainable with vat dyes. A. H.

PATENTS

Printing and Dyeing with Azoic Dye Compositions. FBy. *BP* 715,249

Azoic dyes are produced on the fibre by printing or slop-padding and with simple steaming with neutral steam by using pastes or solutions containing neutral non-volatile alkali salts of the compounds of formula—



(R^1 = H, subst. or unsubst. Alk; R^2 = radical of an amino-alkyl sulphonic or carboxylic acid or Alk containing solubilising groups) and an azoic coupling component. C. O. C.

Multicolour Printing. Dunlop Rubber Co. *BP* 713,248

Rollers or blocks have a multicoloured printing layer formed of a synthetic nitrile rubber blended with a polyvinyl compound and a pigment. They are used by wetting the printing surface and/or the surface to be printed with a suitable solvent, e.g. *cyclo*hexanone or toluene, and then bringing the two surfaces together. Rollers or blocks of this type may be used for printing a wide variety of surfaces particularly natural or synthetic rubber, polyvinyl chloride, fibres of all types, paper, etc. Where absorbent surfaces are being printed a subsequent hot calendering improves the adhesion of the prints, e.g. prints on cloth are rendered faster to washing.

BP 713,264

The printing surface consists of a pigment blended with a rubbery butadiene–acrylonitrile copolymer. This is used to print into a flexible material from which the print is transferred to the material to be printed. The printing surface and/or the flexible sheet and the flexible sheet and/or the final surface are moistened with a solvent before each step in the process. C. O. C.

Multicolour Printing—Detection of Contamination of One Dye by Another. W. Meitner. *BP* 714,757

Contamination of one printing paste by a previously applied paste, especially the one preceding it, is readily detected by making radioactive the paste most liable to cause contamination and using a radiation detector to test the radioactivity of the paste liable to contamination. C. O. C.

Resist-style Prints on Non-cellulosic Textiles. Hardman & Holden. *BP* 715,393

The material is treated locally with an aldehyde (or a substance yielding an aldehyde when heated) either before or after it is impregnated with a vat dye and thiourea dioxide, aged in saturated steam at 100°C. and finally oxidised. The areas where the aldehyde was applied or liberated remain uncoloured. C. O. C.

Printing with Liquids of High or Low Viscosity. McCorquodale Colour Display. *BP* 713,856

The material to be printed is held in a support and is then engaged by a matrix having cavities in its printing surface in such a manner that each cavity forms with the surface to be printed a fluid-tight chamber. A port to each cavity extends through the body of the matrix and is connected with a reservoir of the printing liquid. There are means to control admission of liquid into the cavities and for sucking the air from the cavities after the matrix has made fluid-tight engagement with the material to be printed.

BP 715,066

Means to enable the air to be withdrawn from the space between the cavity and the material to be printed at the same time that the printing liquid is fed in. C. O. C.

Printing with Daylight-fluorescent Compositions. J. L. Switzer and R. C. Switzer. *BP* 714,420

The daylight-fluorescent compositions described in *BP* 672,763 (J.S.D.C., **68**, 327 (1952)) may be printed at high speed with instantaneous drying so that several colours may be applied at one run through the machine, by modifying the multicolour gravure press by supplying it with successive duplicate intaglio rolls, each printing the same ink on the same areas of the web. By using printing inks having the proper proportion of daylight-fluorescent

fluoragent and flash-drying solvents, and then overprinting the same area with the same ink, accurately delineated areas may be rapidly printed. The prints have the desired daylight fluorescence, as each area has several thin coats of the ink separately applied but fused together. C. O. C.

Printing on Superpolyamide Fibres. FH. *BP* 715,170

Sharp prints of excellent penetration are obtained on nylon by use of an aqueous printing paste containing polyvinyl alcohol as the thickening agent. It may be used with all direct printing pastes but if the dyes contain soda ash it is advisable to use a polyvinyl alcohol formed by the incomplete hydrolysis of polyvinyl acetate. With vat dyes no alkali or reducing agent is added to the printing paste but the prints are aftertreated in a bath containing alkali and a reducing agent. C. O. C.

Glossy Metallic or Pigmented Coatings or Prints on Regenerated Cellulose Films. N.V. Kunstzijdespinnerij Nyma. *BP* 713,914

Metal powder or pigment dispersed in an alkaline solution of hydroxyalkyl cellulose, preferably hydroxyethyl cellulose, is applied to the moist regenerated product, after which the hydroxyalkyl cellulose is precipitated. C. O. C.

Coatings and Prints on Ethylene Polymers. Basf. *BP* 714,796

Coatings and prints on ethylene polymers are obtained by use of a solution containing both a vinyl chloride polymer and a resin soluble in alkyl-substituted benzenes. Suitable solvents are alkyl-substituted benzenes, esters, chlorinated hydrocarbons and ketones. The coatings have high film elasticity and adhesion. C. O. C.

Printing on Halogenated Rubber. Dunlop Rubber Co. *BP* 713,250

Halogenated rubber can be printed by using a solid coloured composition containing a polyvinyl compound. The printing surface and/or the surface to be printed are moistened with a volatile mutual solvent. C. O. C.

Electronographic Printing. Huebner Co. *BP* 715,484

In an electronographic printing press discharge and/or attraction electrodes produce electrostatic fields of force of different configuration and character, thus enabling the areas and strengths of the fields of force at the surface of the material upon which the ink is to be deposited to be varied to meet different printing requirements, e.g. reproduction of narrow to wide images, light and heavy images and colour images varying in density in different portions. C. O. C.

Photographic Images by Migratory Transfer. Ozalid Co. *BP* 715,196

In the process of *BP* 654,630 the depth and colour of the transferred image depend largely on the choice of substance used for the development nuclei, and still further deepening of the image can be obtained by incorporating in the transfer material a high energy development. Colloidal hydrated copper sulphide preferably forms the development nuclei and the developer hydroquinone with or without metol. C. O. C.

Cotton Finishing Developments (X below).

X— SIZING AND FINISHING

Cotton Finishing Developments. A. Bolgiani. *Dyer*, **111**, 877–883 (11 June), 955–961 (25 June 1954).

In this paper, presented at the Jubilee International Cotton Congress, a survey is made of technical progress in fibre, sliver, yarn, and piece goods processing. The first section deals with yarn singeing, sizing, automatic yarn-mercerising machines, high-temperature dyeing machines, and the behaviour of dyes at high temperature. Section two is devoted to piece goods; singeing, scouring, bleaching systems, mercerisation, and modern jiggers are surveyed followed by printing, finishing (mechanical, embossed, and resin finishes), and finally a comparison between rubber-belt and felt-blanket compressive shrinking machines. A. H.

Application of Resins to Textiles. A. R. Smith. J.S.D.C., **70**, 381–391 (Sept. 1954).

The nature of thermoplastic and thermosetting resins is discussed together with the chemical reactions involved in their preparation. The application of thermosetting resins to cellulosic fabrics for the production of crease-resistant, dimensionally stable, and permanently glazed and embossed fabrics is outlined, while their use for the prevention of felting in wool fabrics and for the permanent stiffening of various types of textile materials is also considered. The use of thermoplastic resins in the treatment of textiles is discussed, and finally a number of special applications of synthetic resins in the production of permanent showerproof, fire-resistant, and other finishes is briefly outlined. AUTHOR

Mildew-preventing Activity of Rhodanine Derivatives. F. C. Brown, C. K. Bradsher, S. M. Bond, and R. J. Grantham. *Ind. Eng. Chem.*, **46**, 1508–1512 (July 1954).

Certain derivatives of rhodanine have been found to prevent microbiological attack on cotton. The effect of variation in structure on the activity of some related derivatives has been studied, and data are presented on the rotproofing efficiency of 44 rhodanine derivatives and 6 derivatives of dioxothiazolidine. The most efficient compounds were 5-*p*-chlorobenzylidenerhodanine and 5-(2-thenylidene)rhodanine. Cotton impregnated with 1% of these compounds lost respectively 7% and 15% strength after 4 weeks' soil burial. The 5-substituted 2:4-dioxothiazolidines were less effective than the corresponding 5-substituted rhodanines. W. K. R.

Octadecyl *iso*Cyanate as a Water-repellent on Cotton. C. Hamalainen, J. D. Reid, and W. N. Berard. *Amer. Dyestuff Rep.*, **43**, 453–457 (19 July 1954).

A brief survey is given of the use of *iso*cyanates in waterproofing. Experiments have been carried out on cotton linters and cotton fabric with octadecyl *iso*cyanate, and water-emulsion and organic-solvent methods of application are compared. Semi-commercial-scale trials have been made. An uptake of 2–5%, applied by either method, is effective for superficial water resistance if the carrier liquid is evaporated and the fabric cured, washed, and heat-dried. The finish is fast to solvents and laundering, but fails under dynamic water-repellency tests, and is, therefore, only showerproof. It appears that a large part of the repellency is due to the formation of very insoluble dioctadecylurea by hydrolysis of the *iso*cyanate. J. W. B.

Fire- and Water-proof Finishes resistant to Weathering and Washing. K. Quehl. *Teintex*, **19**, 605–619 (Aug. 1954).

Testing methods for fireproofed materials are discussed. A description of the Queco process, which uses two different proprietary products for fireproofing dyed and undyed materials, is given. Aluminium formate is added for simultaneous waterproofing. The results of this process are compared with those of established methods. S. R. C.

PATENTS

Rendering Cellulosic Textiles Crease-resistant and Soft and/or Water-repellent. ICI. *BP* 713,756

The material is impregnated with aldehyde resin-forming components or condensate, dried at $< 100°$C. and then impregnated with a heat-decomposable quaternary ammonium salt, dried and baked. C. O. C.

Crease-resistant Finish. Tootal Broadhurst Lee Co. *BP* 715,201

When textiles containing cellulose organic derivatives obtained by the further esterification of incompletely esterified or etherified organic derivatives of cellulose are treated with steam, preferably at $> 100°$C., or with water, preferably at 100°C., which may contain solutes, they are more resistant to creasing when wet and shed creases when immersed in water better than if merely washed free with warm water of the by-products of esterification. C. O. C.

Linen-like and Similar Finishes on Cotton Cloths. Heberlein & Co. *BP* 715,376

The dry fabric is passed through aqueous caustic potash of $\ngtr 15°$Bé. at $< 0°$C. for 10 sec. to 2 min. and is then finished as usual. Much better linen-like effects are produced than if wet fabric is passed into caustic soda mercerising lye. C. O. C.

Gaseous Treatment *in vacuo* of Wool, Sheepskins, Furs, etc. Wool Industries Research Assocn. *BP* 714,829

When treating wool with gaseous chlorine or bromine by the process described in *BP* 417,719 (J.S.D.C., **61**, 81 (1935)) if the goods are cooled after drying and before admission to the vacuum treatment chamber very little degradation of any non-animal fibre component or of the skin occurs. C. O. C.

Recovery of Solvents used in Long Webs. P. Vial. *BP* 713,612

When coating webs with organic solvent solutions, the coated web is continuously dried by passing it through a hot atmosphere of the solvent vapour, which atmosphere is continuously subjected to condensing action and is at slightly more than atmospheric pressure and free from air or other gas. C. O. C.

Fabric coated with a Heat-reflecting Metallic Material. H. J. Rand. *USP* 2,630,620

One side of the fabric is coated with microscopic or near-microscopic metal flakes oriented so as to lie in the plane of the surface to form a foliated layer thereon. The metal is bonded to the fabric by an organic binding agent. C. O. C.

Nylon Fabric for Use as Flags, Wind Socks, Aircraft-towed Target Drogues, etc. Sucal. *BP* 714,264

An open-weave nylon fabric is treated with a solution of nylon to anchor the threads where they cross over one another and to prevent them fraying if they are broken. C. O. C.

Relief-like Effects on Textiles, Paper, Leather, etc. without Embossing. Grasser & Co. *BP* 714,423

Relief-like effects without embossing are produced on all types of pile or napped fabrics, rough decorating and furnishing materials, leather, wallpaper, etc. by first pressing or calendering the material to render its face smooth. A water-resistant fixative is then applied in a pattern to this surface and the material then wet-processed to restore the original conditions of the non-fixed portions of the surface. Calendering the material between application of the fixative and wet processing results in a product showing highly glossy, fast-embossed or raised-print effects having an imitation-leather or lacquer-like appearance. In such cases, if a metal powder is included in the fixative, effects resembling metal foil bonded to the material are obtained. C. O. C.

Stretched Fabrics containing Thermoplastic Fibres. Celanese Corpn. of America. *BP* 713,367

Novel effects are produced on fabrics whose warp and/or weft consists of thermoplastic fibres by heating them to soften the thermoplastic fibres and then stretching them while the thermoplastic fibres are soft. C. O. C.

Improving the Fastness to Washing of Materials dyed with Sulphur or Vat Dyes (VIII p. 521).
Pigment Printing and Dyeing (IX p. 522).
Coatings and Prints on Ethylene Polymers (IX p. 523).

XI— PAPER AND OTHER CELLULOSIC PRODUCTS

Infrared Spectroscopy of Hydrogen Bonding in Cellulose. H. J. Marrinan and J. Mann. *J. Appl. Chem.*, **4**, 204–211 (April 1954).

The interaction between cellulose and heavy water permits absorptions due to stretching of OH groups in crystalline and amorphous regions to be studied independently. Crystalline regions give several absorption bands in the 3600–3000 cm.$^{-1}$ range, and it is shown that all the bands are due to stretching of OH groups. Arguments are presented in support of the idea that these bands can be interpreted in terms of vibrations of individual groups. It is shown that all the OH groups in crystalline regions of regenerated and bacterial celluloses are hydrogen-bonded and that crystal structures suggested by Peirce for these celluloses are incorrect. Suggestions are made regarding the types of hydrogen bond present in regenerated cellulose. The relationship between infrared absorption frequencies and O . . O distances in crystals is discussed. It is concluded that no reliable estimate of O . . . O distances in cellulose can be made from absorption frequencies on the basis of results at present available. W. R. M.

Dielectric Relaxation in Cellulose containing Sorbed Vapours. R. Seidman and S. G. Mason. *Canadian J. Chem.*, **32**, 744–762 (Aug. 1954).

Dielectric constant and dielectric loss factor have been measured in a dispersion region for a paper of high cellulose content. Equations are derived from which dielectric constant and maximum loss factor of the cellulose are evaluated for varying amounts of sorbed water, methanol, and ethanol. The effect of each of these vapours on the position of the dispersion region has been studied over a range of frequency and at temperatures varying from −58 to +26°C. A typical plasticising action was observed in all cases. W. R. M.

Preparation and Properties of Hydrocelluloses. M. A. Millett, W. E. Moore, and J. F. Saeman. *Ind. Eng. Chem.*, **46**, 1493–1497 (July 1954).

Native, mercerised, and regenerated celluloses have been hydrolysed to uncontaminated hydrocellulose residues representing 5–99% of the starting material by means of a simple percolation apparatus using constant-boiling HCl. Each cellulose gave a characteristic constant rate of hydrolysis over the whole range. No truly limiting degree of polymerisation was reached for any of the celluloses studied, but moisture adsorption by the residues reached a limiting value after approximately half the starting material had been removed. Whilst the concept that hydrolysis proceeds by lateral attack on the crystallites requires a continuous increase in the ratio of surface to volume for the fine structure of cellulose, the observed uniform hydrolysis rates and limiting moisture adsorption suggest a constant ratio. W. K. R.

Alkylation of Cellulose with Esters of *p*-Toluenesulphonic Acid. J. W. Weaver, C. A. Mackenzie, and D. A. Shirley. *Ind. Eng. Chem.*, **46**, 1490–1493 (July 1954).

The use of esters of *p*-toluenesulphonic acid as alkylating agents for cellulose has been studied. Methylation is achieved more efficiently than with dimethyl sulphate, but the reactivity of the esters with alkali cellulose diminishes as the length of the alkyl group increases. Although ethyl and propyl cellulose ethers were prepared, the butyl and phenyl esters produced no etherification. W. K. R.

Surface Tension and Membrane Formation of Cellulose Ethers in Aqueous Solution. J. Stawitz, H. Krämer, and W. Klaus. *Kolloid-Z.*, **133**, 69–76 (Nov. 1953).

In high concentration, methyl cellulose and hydroxyethyl methyl cellulose are surface-active and form a tough elastic surface film. Hydroxyethyl cellulose is weakly surface-active and hardly forms a film, but carboxymethyl cellulose is inactive and does not give a surface film. L. P.

Structural Elements in Lignin. J. Gierer, B. O. Lindgren, and H. Mikawa. *Svensk Papperstidning*, **57**, 633–637 (15 Sept. 1954).

PATENTS

High-gloss Mineral-coated Paper. S. D. Warren Co. *BP* 714,723

Highly polished paper sheet is made by passing paper with a hard, dry, densified, supercalendered coating, containing a hydrophilic swellable component and a finely divided mineral filler, between a pair of rolls, one of which has a highly polished surface, and applying an aqueous swelling agent to the paper as it enters the nip between the rolls, causing the coating to become plastic and receive a surface complementary to that of the polished roll. The glazed paper may be dried by adjusting the temperature of the polished roll to $\not>$ 170°F. immediately before it comes into contact with the coated surface of the paper. S. V. S.

Coated Paper. North American Paper Process Co. *USP* 2,649,386

Production of a paper having a level surface formed of fine coated and uncoated areas of such small dimensions that they are not at first discernible as separate areas, the coating being forced into the paper so as to keep the surface level. This enables economy in the amount of coating agent used. C. O. C.

Record Materials. National Cash Register Co. *BP* 714,657

Modification of *BP* 628,960.

Different areas of the material are coated with different combinations of the solid particulate substances so that different colours are produced in the different areas when they are subjected to marking pressure. C. O. C.

Antistatic Coatings for Cellulose Ester Films. Eastman Kodak Co. *USP* 2,649,374

The condensates of aldehydes with naphthalenesulphonic acids (Ullmann, *Enzyklopädie der technischen Chemie*, 2nd Ed., **5**, 686 (1930): H. Wagner, *Chem. Z.*, **46**, 801 (1922)) especially Tamol NNO and Tamol P applied from aqueous solution yield clear transparent coatings on cellulose ester films to which they impart antistatic properties. C. O. C.

Cellulose Acetate Moulding Powders. Lansil. *BP* 715,015–6

Granular cellulose derivatives are produced by simultaneously injecting liquid precipitant and a solution of a cellulose derivative into a chamber having a baffle in it. This baffle interrupts the flow of liquor, the speed of which is such that vigorous intermingling of solution and precipitates results. When the granular product, mixed with fillers, pigments, etc., is agitated with a liquid containing a plasticiser under such conditions that coalescence or comminution of the cellulose derivative particles is avoided, the product is suitable for extrusion or injection and compression moulding with no afterforming treatment. C. O. C.

Stable Aqueous Dispersions of Cellulose Ethers (III p. 510).
Affinities of the Most Important Dye Groups for Paper Fibres (VIII p. 521).
Glossy Metallic or Pigmented Coatings or Prints on Regenerated Cellulose Films (IX p. 523).

XII—LEATHER; FURS; OTHER PROTEIN MATERIALS

Structure of Collagen. M. L. Huggins. *J. Amer. Chem. Soc.*, **76**, 4045–6 (5 Aug. 1954).

A structure is suggested for that part of collagen responsible for the observed X-ray diffractions. It agrees with all known experimental facts. The sequence of residues is given by the formula $(R^1R^2R^3)_n$ (R^1 = usually a proline or hydroxyproline residue; R^2 and R^3 = other types). The diagram of the probable bond structure is given. The main chain is coiled in a left-handed helix. There are no large holes within the helix, although there appear to be suitable places for some hydrogen-bonded water molecules, perhaps one per group of three residues. C. O. C.

Mucoid Material in Hides and Skins and its Significance in Tanning and Dyeing. D. Burton and R. Reed. *Discussions Faraday Soc.*, (16), 195–201 (1954).

A review of recent knowledge of the interfibrillary material and its significance in leather manufacture. If the mucoid material is not completely removed before tanning, it remains in the leather and interferes with dyeing. W. R. M.

Reaction of Basic Chromium Salts with Hide Protein. K. H. Gustavson. *Discussions Faraday Soc.*, (16), 185–195 (1954).

Interaction of Tanning Materials with Collagen Monolayers. S. C. Ellis and K. G. A. Pankhurst. *Discussions Faraday Soc.*, (16), 170–179 (1954).

Viscometric Study of the Hardening of Gelatin by Chrome Alum. J. Pouradier. *Discussions Faraday Soc.*, (16), 180–185 (1954).

Tanning of Fatty Acid, Amino Acid, and Protein Monolayers by Metal Ions. J. H. Schulman and M. Z. Dogan. *Discussions Faraday Soc.*, (16), 158–170 (1954).

Study of Diffusion Processes in Tanning. D. M. G. Armstrong. *Discussions Faraday Soc.*, (16), 45–58 (1954).

Fur Dyeing. [H. J. Sanders.] *Ind. Eng. Chem.*, **46**, 11 A–13 A (June 1954).

A range of solutions of conventional fur dyes is being marketed in the U.S.A. in 12-oz. pressurised tins for direct application in the form of an aerosol spray. More uniform application without the need of additional spray equipment is claimed. W. K. R.

Physical Chemistry of Dyeing and Tanning—General Introduction (VIII p. 519).

XIII—RUBBER; RESINS; PLASTICS

Improving Stability to Ultraviolet Radiation. [K. J. Bradley.] *Ind. Eng. Chem.*, **46**, 15 A–17 A (July 1954).

Organic compounds capable of absorbing ultraviolet radiation, which have been used successfully in sunburn lotions and preventatives, are finding industrial uses by incorporation into plastics to prevent degradation of polymer and fading of dye, and into varnishes to prevent crazing, caused by exposure to ultraviolet radiation. Among the most effective ultraviolet absorbers are derivatives of *p*-aminobenzoic acid, e.g. ethyl *p*-dimethylaminobenzoate, and of salicylic acid, anthranilic acid, umbelliferone, coumarin, etc. W. K. R.

Free Energy of Formation of the Amide Bond in Polyamides. A. B. Meggy. *J. Appl. Chem.*, **4**, 154–159 (April 1954).

The degree of polymerisation of a polyamide is determined by the equilibrium between carboxyl, amino, and amide groups and water molecules. Equations are deduced for the relationship between the equilibrium constant K_1, the number-average chain length, and the partial pressure of water. Allowance is made for the presence of cyclic monomer, whose amount is determined by an equilibrium constant K_2. The relative values of K_1 and K_2 are discussed for cases where the monomer is capable of forming 5-, 6-, 7-, 8-, or larger-membered rings. From data on polymers of ε-caprolactam, equations are deduced giving the relationship between K_1, K_2, and the temperature. From these the heat of formation ΔH, the entropy ΔS, and the free energy ΔF for the polyamide bond in polyaminocaproic acid are calculated. Assuming that the values for nylon 66 are not greatly different, equations are obtained for the chain length of nylon 66 in terms of the temperature, and the partial pressure of water and also the chain length as a function of temperature in the presence of an aqueous phase. The reaction between CO_2 and a diamine is discussed, and it is shown that conditions are less favourable to the formation of high polymers. The inability of α-amino acids to polymerise directly is due to the large amount of ionic work necessary in adding a single amino acid to a peptide chain. Tripeptides and higher peptides should be able to polymerise. A comparison is made between polyesters and polyamides. The formation of the amide group is accompanied by a large entropy increase, which is probably mainly due to the release of oriented water molecules held by charged carboxyl and amino groups. Polyesters are formed by interaction between uncharged groups, so that the entropy increase will be much smaller and the conditions less favourable to polymer formation. W. R. M.

PATENTS

Colour Master Batches of Plastics, Rubber, Resins, Waxes, Gums, etc. B. F. Goodrich Co. *USP* 2,649,382

Colour master batches of high quality are obtained by milling a pigment, plastic, or other material to be pigmented, a water-soluble solvent for the plastic, and water. The liquid may finally be removed and reused for making another batch. The product may be dried and ground or, especially with inflammable products such as cellulose nitrate, the filter cake may be treated so as to displace the water by a non-aqueous liquid, e.g. an alcohol. The product has high chromaticity and when used to colour plastic masses the full strength of the pigment is realised. Coating compositions in which such products are used are uniformly and highly coloured. Filaments formed by extruding plastics coloured with such products are not only evenly and highly coloured but have unaltered tensile strength and there is no clogging of the spinnerets or dies. C. O. C.

Antioxidant for Rubber. United Kingdom Chemicals. *BP* 714,772

Derivatives of resorcinol having in the 4-position or in the 4- and 6-positions one or two alkyl, aralkyl, *cyclo*alkyl or naphthenic hydrocarbon groups are good antioxidants for natural or synthetic rubbers. C. O. C.

Stabilising Synthetic Linear Polyamides to Heat (VI p. 517).
Solvents for Acrylonitrile Polymers (VI p. 518).
Solvent for Polyacrylonitrile (VI p. 518).
Solutions of Polyacrylonitrile (VI p. 518).

XIV—ANALYSIS; TESTING; APPARATUS

The Physics of Particle-size Measurement. II—Optical Methods and Light Scattering. P. G. W. Hawksley. *Bull. Brit. Coal Utilisation Research Assocn.*, **16**, 117–147, 181–209 (1952).

Review with 227 references. C. O. C.

Rapid Determination of Nitrates and Nitrites. J. L. Nelson, L. T. Kurtz, and R. H. Bray. *Anal. Chem.*, **26**, 1081–1082 (June 1954).

The method is based on the diazotisation of sulphanilic acid (I) by NO_2^-, followed by coupling with 1-naphthylamine (II) to give a red dye, the concn. of which may be measured spectrophotometrically at 520 mμ. When present, NO_3^- is reduced to NO_2^- by powdered Zn (III) and $MnSO_4.H_2O$ (IV), in presence of citric acid (V). The reagents, I–V, are dispersed in powder form in $BaSO_4$, and intimately ground together; in this form the reagent is stable for 2–3 years if properly stored. If NO_2^- is to be determined in presence of NO_3^-, III and IV are omitted from the reagent mixture. The citric acid complexes Fe, which would otherwise interfere. The preparation of the reagent and the test procedure are described fully. The method is easily sensitive to 0·05 p.p.m. of N as NO_3^-, and if test soln. are arranged to contain 0·2–1·0 p.p.m. N in this form, the reproducibility is within $\pm$ 5%. The test soln. must be colourless. J. W. D.

Quantitative Estimation of Aromatic Nitro Compounds. E. Wolthuis, S. Kolk, and L. Schaap. *Anal. Chem.*, **26**, 1238–1240 (July 1954).

Nitro cpd. are dissolved in glacial acetic acid, and reduced to the corresponding amines by means of Zn dust–HCl. The amines may be determined by titration with $NaNO_2$ at room temp. in presence of NaBr (to accelerate the diazotisation); during the titration the pH must be kept at $\not> 3$. Trial determinations of the equiv. wt. of 14 aromatic nitro cpd. showed an average error of $\not>$ 1% in 9 instances, and $\not>$ 2·7% in the remainder. Mononitro compounds give, in general, satisfactory results, but dinitro cpd. in which both NO_2 groups are in the same ring do not, being subject to side-reactions. Negatively substituted amines, e.g. nitroamines, require special precautions. Mononitro cpd. may be qual. detected sensitively by similar reduction and diazotisation followed by coupling with R salt in a filter-paper spot test J. W. D.

Photometric Titrations in Non-aqueous Solvents. C. N. Reilley and B. Schweizer. *Anal. Chem.*, **26**, 1124–1126 (July 1954).

Weak bases such as *o*-chloroaniline and quinoline may be titrated, in glacial acetic acid soln., with glacial acetic acid soln. of $HClO_4$, the titration cell being placed in the light path of a spectrophotometer. The curve of absorbance (at a selected wavelength) *versus* corrected vol. of titrant shows a distinct break at the equivalence point, which agrees well with the potentiometric end-point. A substance whose acidic and basic forms do not absorb in the ultraviolet region, e.g. Na acetate, may be titrated by this method in presence of an absorbing species of weaker basicity, e.g. *o*-chloroaniline. The method is described in detail. J. W. D.

Titration of Aromatic and Aliphatic Amine Picrates in Non-aqueous Solution. J. R. Clark and S. M. Wang. *Anal. Chem.*, **26**, 1230 (July 1954).

Amine picrates (I) may be determined, in glacial acetic acid soln., by titration with $HClO_4$ in the same solvent, using methyl violet as indicator; the yellow colour of the picrates does not interfere with the end-point. Milliequivalent quantities of I are used. Proving analyses are cited. J. W. D.

Benzidine Rearrangement during Titration of Azo Compounds with Titanous Chloride. S. Veibel. *Canadian J. Chem.*, **32**, 638–639 (June 1954).

The benzidine rearrangement which takes place during the titration of certain subst. azobenzenes with titanous salts may occur in nearly neutral soln. strongly buffered with sodium citrate; a strongly acid medium is not essential. Under these conditions azobenzene requires only 2 equivalents of $TiCl_3$. Other azo compounds such as 3-nitroazobenzene and 4-carboxyazobenzene may use rather more than 2 equiv.; when the *para* positions to the azo group are blocked, 3–4 equiv. are required, and a semidine or diphenyline rearrangement may occur in such instances. Titration of *o*-azotoluene in the normal manner requires slightly $>$ 2 equiv. of $TiCl_3$, but when an excess of $TiCl_3$ is added immediately, up to 3 equiv. are needed. This indicates that, when the initial reduction of the azo compound to a hydrazo compound has taken place, two other reactions proceed simultaneously, viz. reduction to an aniline and rearrangement to a benzidine. J. W. D.

Application of Radioactive Tracer Techniques to Textile Research. H. J. White. J.S.D.C., **70**, 284–287 (July 1954).

Some properties of radioactive tracers are reviewed briefly, and the advantages of their unique properties are pointed out. Several applications of tracer techniques to problems dealing with fibres are described. AUTHOR

Rapid Testing of the Stability to Light of Textiles. A. Sippel. *Textil-Praxis*, **9**, 575–576 (June 1954).

Low-pressure mercury-vapour lamps emit ca. 95% at 2537 A., but such light, although present in solar radiation and extremely powerful, is filtered out before reaching the surface of the earth. The effect of such radiation is, unlike sunlight, independent of temperature humidity, or oxygen content. High-pressure mercury-vapour lamps give a more continuous ultraviolet spectrum, but the radiation is still rich below 3000 A., and ultraviolet glass of ca. 2 mm. thickness is used to absorb this portion. The light from several high-pressure lamps is filtered in this manner and allowed to irradiate the patterns, which are maintained in an atmosphere of constant temperature, high relative humidity, and rapid circulation to remove ozone and to produce a cooling effect. The times necessary for the tensile strengths of standards and patterns to fall to 5% of the original value show good correlation between irradiation in sunlight behind window-glass and in the apparatus. S. R. C.

Electron-microscope Study of Cellulose Fibres in Ultra-thin Sections after Treatment with Thallous Ethoxide. (An Attempt to produce a Specific Electron Staining.) S. Asunmaa. *Svensk Papperstidning*, **57**, 367–368 (31 May 1954).

In studying the ultra-fine structure of cellulose, fibre sections 200–300 A. thick have been investigated using Sjöstrand's method and his new microtome for substantially unswollen holocellulose fibres from Swedish spruce. The contrast in the sections was improved by treatment with thallous ethoxide. The distribution of thallium in the fibre sections is demonstrated, and some dimensions are given. S. V. S.

Changes in Cell Wall Dimensions of Carbohydrate Fibres after Esterification with *p*-Phenylazobenzoyl Chloride and Subsequent Swelling in Pyridine. S. Asunmaa and P. W. Lange. *Svensk Papperstidning*, **57**, 498–500 (15 Aug. 1954).

In quantitative microspectrographic work, the relative changes in dimensions of an object due to swelling, etc. must be corrected for. The influence of swelling of the esterified fibres was studied by photomicrographic measurements of the perimeters of the fibre and of the lumen. Comparison of equivalent distances in cross-sections of carbohydrate fibres before and after esterification with *p*-phenylazobenzoyl chloride showed that, within $\pm$ 10%, the relative concentrations of material across the cell wall of the esterified swollen fibre are identical with those across the cell wall of the untreated carbohydrate fibre. S. V. S.

Air-flow Method of Measuring Wool Fibre Fineness. S. L. Anderson. *J. Textile Inst.*, **45**, P312–P316 (July 1954).

A review of the air-flow method of measuring wool-fibre fineness is followed by a detailed description of the apparatus and procedure. Sampling errors are discussed and figures for accuracy given. J. W. B.

Paper-chromatographic Method for the Quantitative Estimation of Amino Acids. A. L. Levy. *Nature*, **174**, 126–127 (17 July 1954).

Amino acids are converted, in aq. soln., to their *N*-2:4-dinitrophenyl (DNP) derivatives; ether extraction removes all DNP deriv. except those of arginine and histidine. Both soln. are applied to paper and irrigated with toluene–chloroethanol–pyridine–0·8N. ammonia; the chromatogram given by the ether extract is run in the second dimension with 1·5M. phosphate buffer. After being cut out, the separate spots are eluted with water at 55–60°C. and the soln. estimated spectrophotometrically at 360 mμ. Full details are given, a diagram of a typical chromatogram is shown, and the application of the method to protein hydrolysates is discussed at length. J. W. D.

New Method for the Colorimetric Estimation of Amino Acids on Paper Chromatograms. F. A. Isherwood and D. H. Cruickshank. *Nature*, **174**, 123–126 (17 July 1954).

The *N*-2:4-dinitrophenyl (DNP) derivatives of amino acids may be separated from the large excess of 2:4-dinitrophenol which originates in the excess of dinitrofluorobenzene (DNFB) required for their complete conversion (and which interferes with the subsequent colorimetric finish), by dissolving the mixture in 91% H_2SO_4 and extracting the dinitrophenol with benzene; the acid soln. is then diluted to 30%, and the DNP derivatives are extracted with *tert.*-amyl alcohol–benzene and transferred to aq. Na_2CO_3 for colorimetric estimation. Levy (previous abstract) merely extracts the excess DNFB from the alkaline reaction mixture, with ether. The recommended procedure, and the work on which it is based, are described in full detail. It is advisable to protect the soln. containing the DNP derivatives from strong light, since they are destroyed by it at a significant rate. J. W. D.

Filament Surface Investigation by a Simple Interferometric Method with particular reference to Nylon Filaments. S. C. Simmens. *J. Textile Inst.*, **45**, T569–T574 (July 1954).

A small piece of nylon filament is supported on a microscope slide in loop form, radius of bend 15 mm. in the vertical plane, and a cover glass is supported above it by means of an extension from the substage condenser. This is carefully lowered until contact is made between the filament and the slip, under which conditions interference fringes are observed under high power, using vertical monochromatic illumination. Photographs are shown of the patterns given by drawn and undrawn nylon; those on the surfaces of undrawn nylon can be ascribed to spherulitic growth. J. W. B.

Polarographic Determination of Amino Acids. D. R. Norton and N. H. Furman. *Anal. Chem.*, **26**, 1116–1119 (July 1954).

Glycine, alanine, tryptophan, aspartic acid, lysine, and histidine have been determined in mg. quantities by means of their reaction with phthalaldehyde. In a borate or CO_3^{2-} buffer at pH 10·5 the reaction is complete in ca. 2 hr. at reactant concn. of the order of 10^{-3}M. The suppression of the reduction current of the second phthalaldehyde wave, under these conditions, $\propto$ [Amino acid]. The amino acids must be separated from NH_3, gelatin, and one another, before reaction. A preliminary study of the reaction between gelatin and phthalaldehyde is reported. The precision of the method is $\sim$ 2% in the 10^{-3}M. range, and this may well hold good at 10^{-4}–10^{-5}M., though it is very unlikely to extend to lower concn. J. W. D.

Separation of Amino Acids by Column Chromatography. R. C. Thomas, V. H. Cheldelin, B. E. Christensen, and C. H. Wang. Northwest Regional Meeting of the American Chemical Society: *Anal. Chem.*, **26**, 1248 (July 1954).

In a typical separation of a complex mixture of amino acids in a protein hydrolysate, a quaternary ammonium base type of resin (IRA-400) column retains all the amino acids except arginine, which passes through together with the acid and basic impurities in the system. The HCl eluate from the column is passed through a weakly basic type of resin (IR-4B) to remove aspartic and glutamic acids, and two buffered carboxylic acid type resins (IRC-50) to remove lysine and histidine individually. The effluent from the last column is chromatographed on Dowex 50 into individual pure amino acid fractions; the alanine and glycine bands overlap somewhat, and serine and threonine are obtained together in their respective fractions. These pairs may be separated by cellulose powder partition chromatography, using butanol for the elution. J. W. D.

Shrinkage in Laundering of Cotton and Rayon Fabrics. AATCC Research Committee on Dimensional Changes. *Amer. Dyestuff Rep.*, **43**, P364–P367 (7 June 1954).

A summary is presented of an exhaustive series of tests made on 16 unshrunk and shrunk woven cotton and rayon fabrics, using eight laboratory washing methods. A comparison is also made with results obtained under domestic and laundering conditions. J. W. B.

Use of Metal Tubes in the Launder-Ometer for the Dynamic Absorption Test. G. J. Mandikos. *Amer. Dyestuff Rep.*, **43**, P402–P404 (21 June 1954).

The use of Launder-Ometer steel tubes in the dynamic absorption test is suggested in view of the availability of the tubes, and of the good agreement of results so obtained with those obtained with the standard apparatus. J. W. B.

Laboratory Apparatus for Detergency Studies. W. A. Straw. J.S.D.C., **70**, 288–293 (July 1954).

An apparatus is described for providing controlled mechanical agitation of chopped fibre in detergent liquors on a laboratory scale, employing relatively low liquor : fibre ratios. Thermostatic temperature control is provided, and by means of calibration graphs, temperature–time conditions can be selected to follow industrial practice. An estimate is given of the accuracy of speed and temperature control. AUTHOR

Direct Colorimetric Determination of Chlorine Dioxide in Water. H. W. Hodgden and R. S. Ingols. *Anal. Chem.*, **26**, 1224–1226 (July 1954).

Chlorine dioxide may be determined by measuring the absorbance at 490 mμ. of the colour produced with tyrosine at pH 4·3–5·2 (optimum 4·6); alternatively, standard cobalt nitrate soln. may be used. The reaction is selective for ClO_2, and is free from interference by HOCl or chloramines. Studies upon which the recommended conditions of reaction are based are fully reported and discussed. For ClO_2 concn. $<$ 0·2 p.p.m. the sensitivity is poor. J. W. D.

Beckman Flow Colorimeter. J. F. Bishop and R. S. White. *Ind. Eng. Chem.*, **46**, 1432–1435 (July 1954).

Continuous colour analysis of a stream of coloured fluid is provided by passing a light beam through a known amount of the liquid in a cell fitted into a sample stream, and then through an appropriate filter. The transmitted light is measured photoelectrically, and the information fed to a remotely positioned amplifier and recorder. The instrument may be adapted for the continuous measurement of turbidity. W. K. R.

Chromatographic Study of the Tinctorial Properties of Acid Dyes. H Egli. *Tinctoria*, **51**, 14–15 (Jan. 1954).

Brief account of a new chromatographic method for determining the dyeing properties of an acid dye in which wool felt is used in a special steam-jacketed column. C. O. C.

The du Pont Jackson Laboratory Package Dyer. R. H. Blaker and T. W. Stricklin. *Amer. Dyestuff Rep.*, **43**, 392–393 (21 June 1954).

A laboratory dyeing machine takes 50–100 g. of fibre at temperatures up to 300°F., at liquor : material ratios of 10 : 1 to 20 : 1. It is of particular value in developing dyeing procedures for the new synthetic fibres. J. W. B.

Chromatographic Method for Testing the Dyeing Properties of Acid Wool Dyes. H. Egli and M. Perrig. *Teintex*, **19**, 417–425 (June 1954).

The migration test has only limited value as a standard of levelling power. When shading at the boil, rate of exhaustion is important, and a method, based on a chromatographic process, has been developed to integrate migration and exhaustion. Discs punched from standard wool felt are packed in a special column to a constant height, liquor is fed to the top of the column from a constant-level reservoir, and the column is enclosed in a heated jacket. The dye liquor containing acid and salt is circulated a number of times. After a given period, the column may be dismantled and the progress of the dye down the wool can be examined by arranging the discs in sequence. Colour plates showing the results of such experiments are included. After the first run of liquor, the top few discs take up all the dye, but subsequent recirculation of the exhausted bath shows a position of maximum strength. The latter may then be plotted against pH, if an initial run with blank, boiling liquor is made to establish pH equilibrium. The effects of salt and levelling agents may also be studied, and the method is not limited to wool or acid dyes. The testing procedure reproduces bulk operating conditions. S. R. C.

Analysis of Dithionite (Hydrosulphite), particularly in controlling Vats. A. Airoldi and F. Marchi. *Tinctoria*, **51**, 43–49 (Feb. 1954).

The volume of oxygen absorbed by a weighed sample of $Na_2S_2O_4$ in presence of a large excess of air is measured in a gas burette connected with the reactor through an air reservoir which supplies the air. The $Na_2S_2O_4$ is then estimated on the basis of the reaction $Na_2S_2O_4 + H_2O + O_2 = NaHSO_3 + NaHSO_4$. Estimation of $Na_2S_2O_4$ in vats is done by treating a measured amount of the liquor with 40% HCHO and 10% acetic acid to stabilise the $Na_2S_2O_4$ and simultaneously precipitating the leuco dye (sometimes addition of NaCl is necessary to avoid formation of a colloidal dispersion of the leuco dye), filtering the precipitate, and titrating the $Na_2S_2O_4$ in the filtrate iodometrically by the standard method. C. O. C.

Quantitative Method using Paper Chromatography for Estimation of Reducing Oligosaccharides. W. H. Wadman, G. J. Thomas, and A. B. Pardee. *Anal. Chem.*, **26**, 1192–1195 (July 1954).

The sugars are allowed to react with *N*-1-naphthylethylenediamine, and the derivatives are separated upon a descending chromatogram using 1-butanol–ethanol–water–ammonia (40 : 12 : 16 : 1) as solvent. The amount of each sugar present may be measured by determining the brightness of fluorescence of the separate spots under ultraviolet radiation; the most accurate results are obtained when the spots are separated by cutting, and the derivatives eluted with a 1% soln. of $Na_3PO_4.12H_2O$. Reaction is not complete, and only 60% of the sugar reacts under the conditions described; this is, however, not disadvantageous if appropriate standards are included on the same paper. The method is not entirely satisfactory for the estimation of monosaccharides. J. W. D.

Inherent Limitations of Psychophysical Scales for Gloss, Transparency, and Diffuse Lightness. R. S. Hunter. Spring Meeting of the Optical Society of America: *Anal. Chem.*, **26**, 786 (April 1954).

The light flux leaving an object in space may vary with directions of incidence and view as well as with wavelength. It is felt by many that there should be specific basic methods for the measurement of gloss and other features attributable to geometric selectivity, analogous to those internationally standardised for colour measurement. Both spectral and geometric selectivity are described by curves, but only with colour is it possible visually to match different spectral distributions with mixtures of only three primary lights and thereby to specify colours in a tridimensional system. There are no visually equivalent mixtures of standard light stimuli for the appearances of objects having different goniophotometric curves, and therefore no single set of scales for the geometric aspects of appearance; instead, there are many different geometric scales, each of which is useful because the numbers it gives correlate with visual ratings of some appearance property of a particular type or class of object. Thus only partial, not absolute, measurements of such geometric attributes are possible. J. W. D.

Variable-angle Glossmeter. R. S. Hunter. Spring Meeting of the Optical Society of America: *Anal. Chem.*, **26**, 786 (April 1954).

Since gloss results from directionally selective reflectance, critical control of the angular conditions of light travel is necessary in all gloss measurements. A new glossmeter allows both axial and field angles to be varied at will. Axial angles of incidence and view are established by the positions of arms extending from two hubs on a central pivot, the hubs being movable in opposite directions and at identical angular rates, thus keeping the angles of incidence and view equal and opposite. The light source, lenses, stops, and receptor photocell are mounted on individual blocks which are attached, as on an optical bench, to the swinging arms. Source and receptor field stops and also the aperture stop are cut into brass plates which may be inserted into slots in these blocks. The apparatus permits gloss measurements by most of the standard methods and by many others which are new. J. W. D.

Angular-dependence Light Scattering—A High-resolution Recording Instrument for the Angular Range 0·05–140°. W. H. Aughey and F. J. Baum. Spring Meeting of the Optical Society of America: *Anal. Chem.*, **26**, 786 (April 1954).

A unique optical instrument for the measurement of light scattering in physically non-homogeneous systems is described. The scattering data provide a basis for the size characterisation of optical inhomogeneities in the radius range 0·1–100 μ. The useful angular range of the instrument extends from ca. 0·05° to 140°. Angular resolution of 0·02° is readily attainable for characterising large inhomogeneities at small angles. Scanning rates are 0·1, 0·4, 1·0, 4·0, and 20° per min. Light intensities varying by a factor of 10^9 are measured through the use of an optical attenuator which facilitates use of a multiplier phototube at a low level of illumination. The phototube output is charted by a special high-impedance recorder having a full-scale sensitivity of 0·004 μa. Angles are marked by an auxiliary pen on the recorder. J. W. D.

Determination of Mercury in Pulp and Paper. O. T. Carlson and P. O. Bethge. *Svensk Papperstidning*, **57**, 405–408 (15 June 1954).

The sample is completely oxidised by boiling with a mixture of $HClO_4$ and H_2SO_4 in a special apparatus in which the vapours evolved are condensed. When oxidation is completed, the condensate and the oxidising mixture are combined and, after dilution with water, brought to pH 1 with NH_3. Oxidising substances still present are reduced with hydroxylamine sulphate. The Hg content of the soln. thus obtained is determined colorimetrically with dithizone by the reversion process of Irving *et al.* The method gives good reproducibility, and the amount of Hg found agrees well with the amount originally added. S. V. S.

Rapid Method for Precipitation Fractionation of Cellulose Nitrate. C. Adolphson and E. G. King. Northwest Regional Meeting of the American Chemical Society: *Anal. Chem.*, **26**, 1247 (July 1954).

Speed is attained by not washing the ppt., while accuracy is maintained by correcting the size and mol. wt. of each fraction for dissolved material in the soln. removed with the ppt. The importance of uniform treatment in the nitration step, and its effect on the reproducibility of the determined D.P. (degree of polymerisation) distribution, are stressed. Reproducibility tests show nearly identical distribution curves for the same nitrate. Results are comparable with those obtained by the summative method. J. W. D.

Shape and Surface Structure of Synthetic Fibres (VI p. 517).
Practical Colour Matching on Anodic Films (VIII p. 521).

MEMBERS' CHANGES OF ADDRESS

Andrew, M. J., formerly of The Orchards, Private Road, Sherwood, Nottingham, to Percy Andrew & Son Ltd., Leen Valley Dyeworks, Bulwell, Nottingham

Baranek, R., formerly of 2 Chaucer Street, Chaucer Villas, Nottingham, to 134 Longford Road, Coventry

Basar, O., formerly of 2 Hepton Grove, Frizinghall, Bradford, to 41 St. Paul's Road, Manningham, Bradford

Boyce, A. E. W., formerly of 14 Lake Street, Magog, Quebec, Canada, to 110 York Street, Napanee, Canada

Carlene, Dr. P. W., formerly of I.C.I. Ltd., "Guessens", Welwyn, Herts., to Imperial Chemical Industries Ltd., "Terylene" Council, Hookstone Road, Harrogate

Crabtree, P. G., formerly of 19 Ravenstone Drive, Sale, Manchester, to 18 Leegate Gardens, Heaton Mersey, Stockport

Dixey, J. A., formerly of "Muirloch", 135 Kilpatrick Gardens, Clarkston, Renfrewshire, to Brotherton & Co. Ltd., Cattells Grove, Birmingham 7

Dudbridge, A. H., formerly of Lynd Hurst, Fieldhead Road, Guiseley, near Leeds, to Hazlehead, Station Road, Menston-in-Wharfedale, Yorks.

Egan, M. J., formerly of 9 Ellastone Road, Pendleton, Salford 6, Lancs., to St. Bonaventure's, Cambridge

Ghoroury, Dr. M. S. El, formerly of 10 Karam Abd El Ady Street, Cairo (Manyal), Egypt, to 18 Toulan Street, Cairo (Manyal), Egypt

Goodwin, J. E., formerly c/o Beida Dyers, S.A.E. P.O. Bag, Alexandria, Egypt, to Wycliffe House, Westbourne Park, Urmston, Lancashire

Hannah, T. B., formerly c/o Steele, 52 Dean Street, Kilmarnock, to 89 Fereneze Avenue, Clarkston, Renfrewshire

Harvey, H. C., formerly c/o Manor House, Key Green, Buglawton, Congleton, Cheshire, to 77 Edinburgh Road, Congleton, Cheshire

Hollis, D. J., formerly c/o Mrs. Goddard, "Kinder Spur", Hayfield, near Stockport, Cheshire, to "The Royal Oak", Cleveland Hill, Tuxford, near Newark, Notts.

Jackson, J. B., formerly of 10 Hall Drive, Alkrington, Middleton, to 36 Ardern Road, Crumpsall, Manchester 8

Laskowska, Mrs. W. B., formerly of 51 Dryden Street, Nottingham, to 8 Regent Street, New Basford, Nottingham

Manitus, L. G., formerly of 254 St. Patrick Street, West, Magog, P. Que., Canada, to 50, 57th Avenue, Pointe aux Trembles, Montreal 5, Quebec, Canada

Marshall, D. G., formerly c/o Yorkshire Dyeware & Chemical Co. Ltd., Export Branch, 65–71 Meadow Lane, Leeds, to c/o The Yorkshire Dyeware & Chemical Co. Ltd., Kirkstall Road, Leeds 3

McCallum, J. G. B., formerly c/o J. & J. McCallum Ltd., Laigh Park Dyeworks, Paisley, Scotland, to c/o J. Turnbull & Sons Ltd., Slitrig Works, Hawick

Pomfret, R. E., formerly of 150 Victoria Street, Magog, P.Q., Canada, to 455 Palace Road, Kingston, Ontario, Canada

Reis, A. A. C., formerly of 17 Marlborough Road, Manningham Lane, Bradford, to 10 Blenheim Road, Manningham Lane, Bradford

Shaw, G., formerly of Public Textile Testing House, 16 Ormeau Avenue, Belfast, to 60 Beresford Avenue, Tolworth, Surbiton, Surrey

Shepherd, E., formerly of 102 Cutler Heights Lane, Bradford 4, to 88 Welbeck Drive, Hollingwood Lane, Bradford 7

Smakowski, L., formerly of 11 Ingram Street, Huntingdon, Hunts., to 21 Clarence Road, Sudbury, Suffolk

Smith, J. V., formerly 120 Trinity Street, Huddersfield, to 267 Bradford Road, Fartown, Huddersfield

Waldeck, A. S., formerly c/o Ciba Co. Ltd., 1235 McGill College Avenue, Montreal, P.Q., Canada, to 10 Royal George Apartments, Regina, Sask., Canada

Waller, 2nd Lt. J., formerly of 4 Chapel Street, Birdwell, Barnsley, to Royal Signals, Officers Mess, 10 B.O.D., MELF 15

White, G. S. J., formerly of 96 Acre Lane, Bramhall, to 53 Moss Lane, Bramhall, Stockport, Cheshire

Wozniczka, T. Z., formerly of 26 Bath Street, Huddersfield, to c/o 51 Woodhouse Hill, Fartown, Huddersfield

NEW MEMBERS AND JUNIOR MEMBERS

Persons desirous of joining the Society as Ordinary Members or Junior Members may obtain Application Forms from the Secretary, or from the Honorary Secretary of any Section of the Society

NEW MEMBERS

Aggarwal, R. R., Niemla Textile Finishing Mills Limited, Chheharta (Amritsar), India

Allison, R. C., 54 Shelbourne Road, Yonkers, New York, U.S.A.

Benjamin, P. M., United Merchants and Manufacturers Inc., 1407 Broadway, New York, N.Y., U.S.A.

Bennett, C. B., Clayton Dyestuffs Co. Limited, Bush House, Aldwych, London WC2

Ginnochio, J. C., 40 Spring Gardens, Didsbury, Manchester 20

Grosbein, P., Provincial Institute of Textiles, 196 Wentworth Street, Hamilton, Ontario, Canada

Illingworth, E. R., c/o I.C.I. (India) Limited, P.O. Box 130, Madras, India

Kaye, L., New Fibres Section, Dyehouse Dept., I.C.I. Limited, Hexagon House, Blackley, Manchester 9

McErlean, J., 41 Bontine Avenue, Brucehill, Dumbarton, Scotland

Nadkarni, P. S., Imperial Chemical Industries Limited, Dyestuffs Division, Hexagon House, Blackley, Manchester 9

Stocker, D. E., Springfield Hosiery Finishing Co. Ltd., Hucknall Lane, Bulwell, Notts.

Watson, J., 33 Fullarton Drive, Troon, Ayrshire

Young, D. T., 34 Fairfield Road, Toller Lane, Bradford 8

NEW JUNIOR MEMBERS

Brown, A. J., 8 Melton Road, off Bury Old Road, Manchester 8

Liddle, L., Provincial Institute of Textiles, 196 Wentworth Street N, Hamilton, Ontario, Canada

ADDRESSES WANTED

Bryne, L. F., formerly c/o Wm. Walker & Sons Ltd., Research Dept., Rose Hill Tannery, Bolton, Lancs.

Nayar, K. N. S., formerly c/o U. T. M. Ltd., Anchor Mills, Paisley, Scotland

Nixon, I. G., formerly of Adriaan Goekooplaan, 105 Flat Gebouw Catsheuvel, The Hague, Holland

Salomon-de-Freidberg, J. A., formerly of 11a Wiverton Road, Sherwood Rise, Nottingham

SITUATIONS VACANT AND WANTED *etc*

Replies may be addressed "Box —, SOCIETY OF DYERS AND COLOURISTS," DEAN HOUSE, 19 PICCADILLY, BRADFORD 1, YORKS., where all communications relating to these Advertisements, which are treated in strict confidence, should be addressed.

The Publications Committee is prepared to receive Advertisements relating to SITUATIONS VACANT, SITUATIONS WANTED, or MISCELLANEOUS ITEMS for insertion on this page of the Journal. Advertisements of Situations Wanted are gratis to individual members, but must not exceed twenty-four words in length.

All inquiries relating to Advertisements in the Journal should be addressed to THE SECRETARY, THE SOCIETY OF DYERS AND COLOURISTS, DEAN HOUSE, 19 PICCADILLY, BRADFORD 1, YORKS.

SITUATIONS VACANT

The engagement of persons answering these advertisements must be made through a Local Office of the Ministry of Labour or a Scheduled Employment Agency if the applicant is a man aged 18–64 inclusive or a woman aged 18–59 inclusive unless he or she, or the employment, is excepted from the provisions of the Notification of Vacancies Order 1952.

AUSTRALIA. Combing Manager required by old-established firm near Sydney for merino and fine crossbred plant. Experience of French combing an advantage. Write giving full details as to age, qualifications, experience and salary level to Box V56.

AUSTRALIA. Dyer wanted to take charge of wool top and yarn Dyehouse for old-established firm near Sydney. Write giving details of age, qualifications, experience and salary level to Box V57

DYER CHEMIST wanted to take control of Dyehouse dealing with a wide range of Ladies' and Gents' Woollen and Worsted Suitings, Gaberdines etc., also loose wool. Salary according to ability and experience. Write in confidence to Box 6314 Williams's Advertisement Offices, Bradford.

IMPORTANT French firm for printing on cotton is requiring well-trained Chemical Engineer with practical experience to assist Manager of rollers printing works. Replies to be sent to Gillet-Thaon à Thaon-les-Vosges (Vosges), France.

REQUIRED FOR MIDDLE EAST (not Egypt) suitably qualified person of middle age with long practical experience to take charge of medium size bleaching, dyeing and finishing plant producing cotton and rayon textiles. Knowledge all three functions required but especially strong in dyeing on jig, winch, open beck and pigment padding. Some theoretical knowledge an advantage. Please reply giving details of age, composition of family, state of health, qualifications and experience with copy references which will be treated confidentially. Good salary and conditions to right man. Apply Box V58

TEXTILE CHEMIST required to be responsible for the general control of processing in Bleach and Dye Works. Experience of package dyeing of fast colours is essential, and some experience of piece dyeing is preferred. Please apply in writing giving details of age, experience, and qualifications to the Manager, Vantona Textiles Limited, Ainsworth Mill, Breightmet, Bolton, Lancs.

BRITISH RAYON RESEARCH ASSOCIATION

TEXTILE TECHNOLOGIST required for liaison work with member firms engaged in dyeing, printing, and finishing. Must have had good experience in this branch of the industry and have been concerned with the practical application of the results of research. Applications, with full particulars, should be addressed to the Secretary British Rayon Research Association, Heald Green Laboratories, Wythenshawe, Manchester.

WHIFFEN & SONS LIMITED, a member of the Fison Group of Companies, have a vacancy on their technical selling staff for a man to assist develop a range of textile chemicals. Knowledge of selling and of the textile industry are important, and applicants should preferably have a chemical qualification.

Salary will be according to age and qualifications; car provided, pension scheme. Apply The Sales Manager, Whiffen & Sons Limited, North West House, Marylebone Road, London N.W.1.

SITUATIONS WANTED

CHEMIST COLOURIST, Inter. Science, Diploma in dyeing and finishing and three Full Tech. Certificates C.G.L.I. Dyeing of Textiles, wide experience hank, sliver and beam pressure dyeing desires post as technical adviser or Manager, also abroad. Several languages. Box W530

MEMBER desires fresh scope. Fully experienced in all dyeing methods full scale and Lab. technical representation home and abroad. Usual tech. training and up to date. Reply Box W531

FORTHCOMING MEETINGS OF THE SOCIETY — *continued from page x*

Thursday, 10th February 1955
WEST RIDING SECTION. Details Later.

Tuesday, 15th February 1955
HUDDERSFIELD SECTION. *Non-Textile Uses of Dyestuffs.* J. P. Gill, Esq., B.Sc. (Imperial Chemical Industries Ltd.). Joint meeting with Huddersfield Section of the Royal Institute of Chemistry. The Co-operative Society Cafe, Buxton Road, **Huddersfield.** 7.30 p.m.

SCOTTISH SECTION. *pH in the Textile Industry.* T. Green, Esq., A.M.C.T. (Clayton Dyestuffs Co. Ltd.). St. Enoch Hotel, **Glasgow.** 7 p.m.

Friday, 18th February 1955
MANCHESTER SECTION. *The Soiling of Synthetic and Natural Fibres.* G. G. Taylor, Esq., B.Sc., A.Inst.P. (Clayton Dyestuffs Co. Ltd.). Textile Institute. 6.30 p.m.

Monday, 21st February 1955
BRADFORD JUNIOR BRANCH. Messrs. I.C.I. Ltd. and Petroleum Film Bureau. Film Evening.

Wednesday, 23rd February 1955
MIDLANDS SECTION. *The Classification of Dyestuffs by their Dyeing Characteristics.* W. Beal, Esq., B.Sc. Kings Head Hotel, **Loughborough.** 7 p.m.

Thursday, 24th February 1955
WEST RIDING SECTION. *Heat Sensitivity of Anthraquinone Acid Wool Dyes.* Dr. R. H. Peters and Dr. T. Watson (Messrs. I.C.I. Ltd.). The Victoria Hotel, Bridge Street, **Bradford.** 7.30 p.m.

Friday, 25th February 1955
MANCHESTER SECTION. Annual Dance.

March 1955
LONDON SECTION. The London Lecture. Details later.

Tuesday, 1st March 1955
LEEDS JUNIOR BRANCH. *The Application of Azoic Dyes to "Terylene" Polyester Fibre at 100-130° C.* H. R. Hadfield, Esq., M.Sc. (Messrs. I.C.I. Ltd.). Departmental Lecture Theatre, The University, **Leeds.** 3.30 p.m.

MANCHESTER JUNIOR BRANCH. *Synthetic Fibres in the Hosiery Industry.* Member of the staff of Clayton Dyestuffs Co., Manchester. (To be announced later). College of Technology, **Manchester.** 6.30 p.m.

Friday, 4th March 1955
MIDLANDS SECTION. MIDLANDS SECTION DINNER. Kings Head Hotel, **Loughborough.** 7 p.m.

Wednesday, 9th March 1955
NORTHERN IRELAND SECTION. Film Evening. (Joint Meeting with Textile Institute). Thompson's Restaurant, Donegall Place, **Belfast.** 7.30 p.m.

Thursday, 10th March 1955
MIDLANDS SECTION. *The Diffusion of Vat Dyes into Cellulose.* R. H. Peters, Esq., Ph.D., F.S.D.C., and T. Watson, Esq., Ph.D. (Dr. Peters lecturing). Gas Theatre, **Nottingham.** 7 p.m.

WEST RIDING SECTION. Title Later. Dr. F. F. Elsworth (Wool Industries Research Association). The Victoria Hotel, Bridge Street, **Bradford.** 7.30 p.m.

Tuesday, 15th March 1955
HUDDERSFIELD SECTION. *Sulphur Colours for Special Purposes.* H. Senior, Esq. (James Robinson & Co. Ltd.). Preceded by Annual General Meeting, Princess Cafe, **Huddersfield.**

LEEDS JUNIOR BRANCH. *The Classification of Dyes by their Dyeing Characteristics.* W. Beal, Esq., B.Sc. (The Geigy Co. Ltd.). Departmental Lecture Theatre, The Univeristy, **Leeds.** 3.30 p.m.

SCOTTISH SECTION — LADIES' EVENING. *The Hand Printing of Textiles.* E. S. Beton, Esq. (Brocklehurst, Whiston Amalgamated Ltd.). Institution of Engineers & Shipbuilders, **Glasgow**. 7 p.m.

Thursday, 17th March 1955
BRADFORD JUNIOR BRANCH. *Dyeing and Finishing of Acetate Woven and Knitted Fabrics.* R. J. Mann, Esq., B.Sc. (British Celanese Ltd.). **Bradford** Technical College. 7.15 p.m.

Friday, 18th March 1955
MANCHESTER SECTION. One Day Symposium. Full details later.

Thursday, 24th March 1955
WEST RIDING SECTION—ANNUAL GENERAL MEETING. The Victoria Hotel, Bridge Street, **Bradford**. 7.30 p.m.

Tuesday, 5th April 1955
SCOTTISH SECTION — ANNUAL GENERAL MEETING. 7 p.m. *Primitive and Modern Dyeing Practice.* (Illustrated) (I.C.I. Ltd.). St. Enoch Hotel, **Glasgow.** 7.30 p.m.

Wednesday, 6th April 1955
MIDLANDS SECTION. Paper by G. H. Lister, Esq., B.Sc., Ph.D. (Subject later) (ANNUAL GENERAL MEETING at 6.30 p.m.). Kings Head Hotel, **Loughborough.**

Friday, 15th April 1955
MANCHESTER SECTION — ANNUAL GENERAL MEETING. Full details later.

Thursday, 21st April 1955
MIDLANDS SECTION. *Some Experiences of a knitted-goods dyer.* A. W. Carpenter. (Joint Meeting with the Textile Institute Kidderminster Section). Carpet Trades Canteen. Mill Street, **Kidderminster.** 7 p.m.

The Society of Dyers and Colourists

★

Annual Dinner

on

1st April 1955

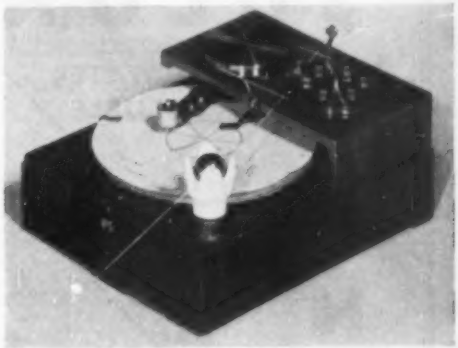
at the

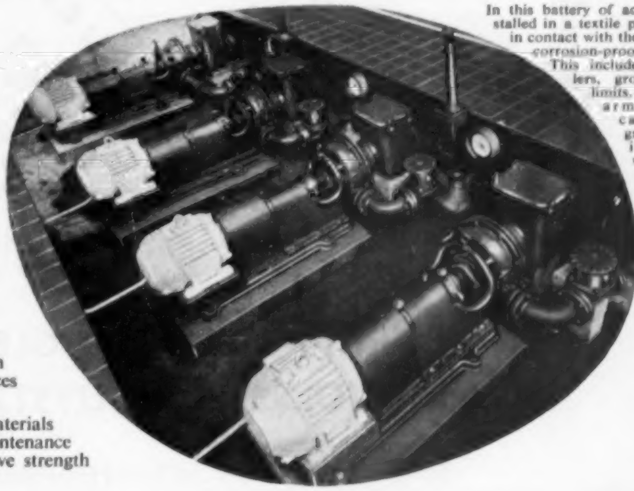
Queens Hotel Leeds

★

As accommodation at the Queens Hotel is now **fully booked** for the above function, intending visitors are advised to contact the Hotel Metropole (*Telephone* Leeds 20841) which is nearest to the Queens Hotel, or the Great Northern Hotel (*Telephone* Leeds 30431).

Advance ticket reservations are invited by letter addressed to the Society.





Notice to Authors of Papers

The MSS. of all papers communicated to or read before the Society become the property of the Society. They should be addressed to the Editor, Society of Dyers and Colourists, 19 Piccadilly, Bradford 1. Authors must not allow their papers to be published elsewhere before they have appeared in the Society's *Journal*. Should prior publication take place without the sanction of the Publications Committee, the paper will be printed only as an abstract or summary.

Manuscripts submitted for publication in the *Journal* should be typewritten (double spacing) on good-quality paper, using one side of the paper only and leaving a margin at least 1 in. wide on the left-hand side. The time taken in refereeing papers (both lectures and communications) will be reduced to a minimum when authors submit two copies of the typescript.

In view of the high costs of publication, it is essential that authors should be as concise as possible. When experimental procedure has already been published, a literature reference to the paper containing the details is sufficient, whilst well known experimental methods should be described very briefly.

Introductory paragraphs describing the aims of the investigation and the method of attack are desirable, and should be followed by the experimental results and their discussion. There should be a brief summary for insertion at the beginning of the paper. References to the literature should be numbered consecutively, using superscript numbers without brackets immediately following the text words or author's name to which they refer.

The list of references should be given at the end of the manuscript and the abbreviations used should be, as far as possible, those given in the "List of Periodicals Abstracted" included at the end of the Index to the preceding year's *Journal*. Reference numbers in this list should be neither enclosed in brackets nor followed by full-stops. As far as possible throughout the manuscript the abbreviations listed in the Jan. 1950 issue (p. 54) should be used. Tables should be numbered consecutively in Roman numerals and Figures in Arabic numerals.

The number of figures and graphs should be kept as low as possible, and data should be presented in the form of either tables or graphs, not both. Drawings should be carefully prepared, preferably in Indian ink, on plain white drawing paper or, preferably, Bristol board. In graphs, the frame and actual curves should be ruled and inked more heavily than any co-ordinate lines, and the latter should not be close together as in ordinary graph paper. Experimental points should always be given, and where several graphs appear in a single Figure clear means of differentiation must be adopted. All numbers and legends are set up in type by the printer, and authors should therefore indicate them lightly in pencil.

Twenty-five free copies of a reprint are supplied to the author of an original paper published in the *Journal*, or fifty free copies are supplied when there are two or more authors, and a further number may be purchased from the Society at the rates given below.

REPRINTS OF LECTURES AND COMMUNICATIONS

Reprints of all lectures and communications are available after publication to members and non-members of the Society. The charges (postage included) are as follows— Single copies 2s. 6d. each; per dozen copies up to and including 8 pages, 12s. 6d., and for papers occupying more than 8 pages of the *Journal*, 17s. Orders should be addressed to "The Society of Dyers and Colourists, 19 Piccadilly, Bradford 1". They can be accepted only if accompanied by remittance and if received immediately after publication of the paper.

PUBLISHED FOR THE SOCIETY AND PRINTED BY CHORLEY AND PICKERSGILL LTD LEEDS
ENTERED AT THE NEW YORK POST OFFICE AS SECOND CLASS MATTER